Europäisches Patentamt

European Patent Office

Office européen des brevets



(1) Publication number:

0 665 138 A2

(12)

## **EUROPEAN PATENT APPLICATION**

(1) Application number: 94120732.6

(a) Int. Cl.<sup>6</sup>: **B60R 21/26**, F42B 3/02, C06C 7/00

② Date of filing: 27.12.94

Priority: 28.12.93 JP 353718/93 07.07.94 JP 180570/94

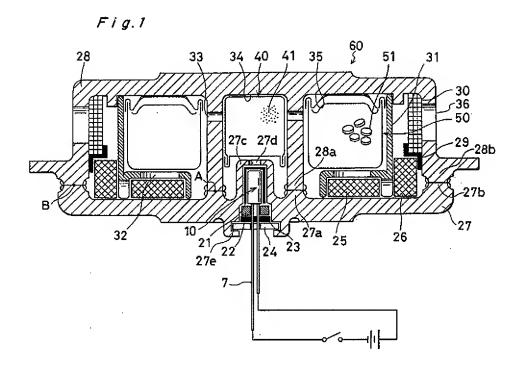
- ② Date of publication of application: 02.08.95 Bulletin 95/31
- Designated Contracting States:
   DE FR GB IT SE
- Applicant: SENSOR TECHNOLOGY CO., LTD. 5-5, Takatsukadal 1-chome Nishi-ku, Kobe-shi Hyogo 651-22 (JP) Applicant: NIPPON KAYAKU KABUSHIKI KAISHA 11-2, Fujimi 1-chome Chlyoda-ku Tokyo 102 (JP)
- Inventor: Yuji, Ito, c/o Himeji Fact. of Nippon Kayaku K.K. 3903-39, Toyotomi, Toyotomicho Himeji-shi, Hyogo 679-21 (JP) Inventor: Ayumu, Kimura, c/o Himeji Fact of Nippon K. K. 3903-39, Toyotomi,

Toyotomicho Himeji-shi, Hyogo 679-21 (JP) Inventor: Masaharu, M., c/o Asa factory of Nippon Kayaku K.K 2300, Ooazakoori, Sanyo-cho Asa-gun, Yamagushi 757 (JP) Inventor: Eishi, Sato, c/o Himeji Fact of Nippon Kayaku K.K. 3903-39, Toyotomi, Toyotomicho Himeji-shi, Hyogo 679-21 (JP) Inventor: Michihisa, T., c/o Himeji Fact of Nippon Kayaku KK 3903-39, Toyotomi, Toyotomicho Himeji-shi, Hyogo 671-21 (JP)

- Representative: Pellmann, Hans-Bernd, Dipl.-Ing. et al Patentanwaltsbüro Tiedtke-Bühling-Kinne & Partner Bavariaring 4 D-80336 München (DE)
- Gas generator, squib for air bag and spontaneous firing explosive composition.

EP 0 665 138 A2

The present invention is a gas generator for air bag comprises a spontaneous firing explosive composition in which at least one of a squib 10, igniting agents 41 and a gas generant 51 contained in a casing 27 or 28 formed of a light alloy material or the like, a spontaneous firing explosive composition consists of carbohydrates, oxyhalogenates and metal oxides and alternatively of carbohydrates, oxyhalogenates, metal oxides and a synthetic resin. The spontaneous firing explosive composition has a spontaneous firing property in temperatures range of 165-220 °C or of 165-200 °C. The carbohydrates is a gaseous component and the oxyhalogenates is an oxygen supplying component. Accordingly, a firing temperature in a relatively low temperatures range of 165-220 °C or of 165-200 °C may be selected depending on combinations of the two. The metal oxides is a heat stabilizer and the synthetic resin is a binder for use in granulating the spontaneous firing explosive composition.



## BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION:

The present invention relates to a gas generator for air bag with a spontaneous firing function which fires at a predetermined temperature to prevent breakdown of a casing when the gas generator for air bag is heated by, for example, flame from outside. And also, The present invention relates to a squib suitable for a gas generator with a spontaneous firing function.

### DESCRIPTION OF THE PRIOR ART:

50

Conventionally, a passive safety device for a vehicle is known that inflates an air bag with gas generated by a gas generator to ensure safety of an occupant when a vehicle is involved in collision. The gas generator comprises a gas generant, an igniting agent for igniting said gas generant and a squib for initiating said igniting agent which are contained in a casing. It is not always necessary to coexist the squib with the igniting agent, and either one of them is used as a case may be. In such a case, one has a function of the other. In addition, said casing is typically made of a light alloy material such as an aluminum alloy with demands for weight reduction.

Light alloy materials are reduced in mechanical strength when heated to a high temperature. Accordingly, a gas generator in which such material is used for the casing will cause no problem in a normal case where the igniting agent is initiated by the squib upon collision and the gas generant is then ignited to generate gas. However, when heat is applied from outside on fire in a vehicle or a warehouse that is not expected in a normal condition, in this event, if a spontaneous firing temperature of the igniting agent or the gas generant is higher than a temperature at which the mechanical strength of the casing is deteriorated, firing is caused after the mechanical strength of the casing is deteriorated. As a result, the casing is broken due to the pressure caused within the gas generator with a risk of its scattering as small pieces.

Against this problem, U.S. Patent No. 4,561,675 discloses a technique relating to an auto ignition device. The an auto ignition device has a primary firing agent that will fire spontaneously at a temperature of approximately 177°C at which the mechanical strength is not deteriorated in a metal container. The metal container is a single independent member made of a metal foil and fixed to an inside of a casing of a gas generator with a heat resistant adhesive or a cushion. And a firing direction of the primary firing agent is directed to a igniting agent or a gas generant that fire at a temperature of approximately 343 °C.

In addition, Japanese Patent Laid Open No: 2-74441 discloses a technique relating to an auto ignition device. The auto ignition device has a primary firing agent that will fire spontaneously at and around a temperature of approximately 160 °C to 180 °C. The primary firing agent casing is inserted to an opening portion of a casing for a gas generator through an insulating material.

Further, Japanese Patent Laid Open No. 5-229397 discloses a technique relating to another auto ignition device. This auto ignition device applies a spontaneous firing agent to an explosive within a squib. The a spontaneous firing agent comprises sulfur-containing binder/sodium perchlorate as a major component that fire spontaneously in 3 minutes at 150-300 °C.

Typical gas generants apply agents based on sodium azide. These agents have an adequate burning rate and a long-term stability when being subjected to a high or low temperature environments. An spontaneous firing temperature thereof is, however, as high as 400 °C or higher. The mechanical strength of the light alloy material such as an aluminum alloy is significantly reduced at that temperature, so that the casing will be broken.

In addition, the igniting agent is typically sealed in an igniting agent container. The igniting agents apply mixtures of boron and potassium nitrate, which will be fired spontaneously at approximately 500 °C. The mechanical strength of the light alloy material such as an aluminum alloy is significantly reduced at that temperature.

Typical squib has a structure in which an explosive is filled within a squib cup of a cylindrical shape with a bottom, which the cup is sealed with a squib plug having a bridge wire for heating which is connect to exterior through a couple of lead pins and the explosive contacts with the bridge wire. The explosive filled within the squib commonly apply mixtures of perchlorate and an organic material or metal powder by the considerations of good initiatability and stability. When heated suddenly from outside, lead trinitroresor-cinate/potassium perchlorate for example will be fired spontaneously at approximately 270 °C while zirconium/potassium perchlorate will be fired spontaneously at approximately 350 °C. As other explosives to be filled in the squib, U.S. Patent No. 3,773,351 discloses those comprising sucrose and potassium chlorate.

In the gas generators disclosed in said U.S. Patent No. 4,561,675 and Japanese Patent Laid Open No. 2-74441, there is a disadvantage that it is necessary to form a containing portion specifically for the auto ignition device in the gas generator. In the gas generator disclosed in Japanese Patent Laid Open No. 5-229397, the spontaneous firing material also serving as the igniting agent is applied to the explosive for the ignitor. The bridge wire contacting therewith is corroded due to acidic substances generated as a result of deterioration with time. There's thus some fear of incorrect operation with the ignitor not initiated upon a normal operation. The squib disclosed in U.S. Patent No. 3,773,351 uses the explosive comprising the sucrose and the potassium chlorate, so that it apparently has an spontaneous firing capability at and around 180 °C. However, thermal stability is not good. More specifically, it does not pass a heat aging test criteria at and around 100 °C such as 107 °C × 400 hours, so that it cannot be applied in practice. In addition, spontaneous firing materials conventionally used are lack of high-temperature stability. Further, those serving also as the igniting agents have a disadvantage of lacking a necessary burning rate.

In particular, those with the squib containing the spontaneous firing material has such a structure that the squib is contained within the gas generator, which makes heat be less likely to be transferred. As a result, there is a disadvantage that it will not be fired spontaneously in a predetermined temperature range in response to application of heat from outside. This problem is the one that may be caused in a case where the spontaneous firing material is contained in the gas generant or the igniting agents.

The present invention is made with respect to these problems inherent to the prior art, and an object thereof is to provide a safe and positive gas generator for air bag which is to be fired spontaneously in a predetermined temperature region in response to application of heat from outside even when the gas generator for use in deploying an air bag as a passive safety device contains a spontaneous firing material in at least one of a squib, an igniting agents and a gas generant, and which maintains stable properties when exposed and being subjected to a high temperature environments for a long time.

In addition, it is also directed to provide an optimum squib incorporated in such a gas generator for air bad.

### SUMMARY OF THE INVENTION

25

A gas generator for air bag according to the present invention directed to achieve the above mentioned object comprises a spontaneous firing explosive composition, which at least one of a squib, an igniting agent and a gas generant contained in a casing formed of a light alloy material includes. The spontaneous firing explosive composition consists of carbohydrates, oxyhalogenates and metal oxides and has a spontaneous firing property in a temperature range of 165-220 °C. As a spontaneous firing explosive composition is in environments where heat is less likely to be transferred from its surroundings, a synthetic resins is further added. In that case the spontaneous firing explosive composition consists of carbohydrates, oxyhalogenates, metal oxides and a synthetic resins. This may have a spontaneous firing property in a lower temperature range of 165-200 °C. In addition, the above mentioned explosive composition that is contained in either one of the squib, the igniting agent and the gas generant will be fired spontaneously in the above mentioned temperature range before a mechanical strength of the casing is deteriorated due to heating from outside.

The carbohydrates in said spontaneous firing explosive composition is a gasifying component, the oxyhalogenates is an oxygen supplying component, the metal oxides is a heat aging agents (thermal stabilizer), and the synthetic resins is a component contributing to improvement of a heat conductivity between these explosive composition particles. Accordingly, an spontaneous firing temperature of 165-220 °C may be selected optionally by means of combining them.

In particular, a gas generator for air bag mounted on a vehicle may be stood at a high-temperature position for a long time such as an outdoor parking place in summer or a tropical area. Accordingly, a high-temperature stability is essential. The one contributing to this thermal stability is said metal oxides. In particular, the thermal stability is improved by means of coating carbohydrates or/and oxyhalogenates particles to avoid direct contact between them. In addition, a synthetic resins has an effect of decreasing a spontaneous firing temperature by means of contacting intimately the above mentioned explosive composition particles with each other so as to improve the heat conductivity between the explosive composition particles.

To achieve a desired spontaneous firing temperature of 165-220 °C or 165-200 °C as well as an adequate burning rate, carbohydrates is preferably 95.0-1.0% by weight, oxyhalogenates is preferably 95.0-1.0% by weight and metal oxides is preferably 30.0-0.01% by weight. A synthetic resins, if added thereto, is preferably 0.05 to 20.0% by weight. This composition ratio may be varied within the above mentioned

composition range depending on a burning rate suitable for a desired part of the gas generator, based on a stoichiometric ratio required for burning carbohydrates and oxyhalogenates. In particular, metal oxides is preferably 30.0-0.01% by weight and more preferably 10.0-1.0% by weight. This may be varied advantageously to adjust the burning rate depending on an internal structure of the gas generator used. With carbohydrates out of this range, the burning rate will be abnormal. With oxyhalogenates out of this range, the spontaneous firing function will be deteriorated. With metal oxides out of this range, the heat aging property and the spontaneous firing function will be deteriorated. If the synthetic resins which adjust the heat conductivity between the explosive composition particles is out of this range, a spontaneous firing temperature will change significantly depending on a degree of mixing.

A particle diameter of carbohydrates, oxyhalogenates and metal oxides significantly affects a positive firing and the high-temperature stability. An average particle diameter of carbohydrates is preferably 0.5 mm to 0.0001 mm. An average particle diameter of oxyhalogenates is preferably 1.0 mm to 0.0001 mm. A particle diameter of metal oxides is preferably 0.5 mm or smaller. With carbohydrates having the particle diameter of out of this range, the heat aging property will be deteriorated. With oxyhalogenates having the particle diameter of out of this range, the burning rate will be abnormal. With metal oxides having the particle diameter of out of this range, the heat aging property and the spontaneous firing function will be deteriorated. In particular, the particle diameter of metal oxides is preferably 1/10 or smaller than the particle diameter of carbohydrates.

It is possible to ensure the positive firing and the high-temperature stability when the average particle diameter of metal oxides is 1/10 or smaller than the average particle diameter of at least one of carbohydrates and oxyhalogenates and when at least one of carbohydrates and oxyhalogenates is coated with metal oxides. A method of coating may be as follows: At first, carbohydrates is mixed with metal oxides to coat metal oxides on a surface of carbohydrates. In another vessel, oxyhalogenates may be mixed with metal oxides to coat metal oxides on a surface of oxyhalogenates. Subsequently, they are mixed with each other. This operation improves the high-temperature stability. The burning rate can be adjusted by an amount of coating.

When the average particle diameters of the individual components are all 0.05 mm or smaller, these three components may be mixed simultaneously.

Of the individual components, applicable carbohydrates may be a single or a mixture of sucrose, lactose, glucose, powder cellulose, dextrin and wood powder. It is preferable to use sucroseas the one having the preferable spontaneous firing temperature of 165-200 °C or 165-220 °C.

Of the individual components, applicable oxyhalogenates include chlorates and perchlorates such as potassium chlorate, potassium perchlorate, sodium chlorate, sodium perchlorate, barium chlorate and barium perchlorate; bromates and perbromates such as potassium bromate, potassium perbromate, sodium bromate and sodium perbromate; and lodates and perlodates such as potassium iodate, potassium perlodate, sodium lodate and sodium periodate. Chlorates and perchlorates are particularly preferable by the consideration of easy handling. Potassium chlorate and potassium perchlorate are more preferable.

Of the individual components, applicable metal oxides include magnesium oxide, calcium oxide, zinc oxide, potassium oxide, sodium oxide and cesium oxide. Magnesium oxide, calcium oxide and zinc oxide are preferable by the consideration of easy handling. In addition, light magnesium oxide is particularly preferable in view of its fine and uniform particle diameter.

Of the individual components, applicable synthetic resins include silicon resins, urethane resins, polyesters, acrylic resins and butyl rubbers. A one component room temperature vulcanizing silicone resin is particularly preferable by the considerations of easy handling and thermal stability. It is noted that granulation is made by means of mixing carbohydrates, oxyhalogenates and metal oxides with each other, to which the synthetic resins is added.

In particular, when the spontaneous firing explosive composition having the above mentioned components is contained in the gas generant, it may be subjected to making tablet or formed into pellets by using an adequate binder to adjust the burning rate, if necessary. In addition, it may be possible to add adequately inorganic powder such as talc, alumina oxide and silicon dioxide as well as organic powder such as wood powder, synthetic resins powder and rosin powder to adjust the burning rate.

In particular, as an aspect of containing the spontaneous firing explosive composition having the above mentioned components in the squib, it may contact directly with the bridge wire. However, in a case where an extremely short firing time is preferable, it is preferable to form a layer structure where an initiating agent is contacted with the bridge wire, and the spontaneous firing explosive composition having the above mentioned components contacts with that initiating agents. Such squib is a single product applicable generally to a part where a spontaneous firing function is required.

As such initiating agent, metal powder/KClO<sub>4</sub>, diazodinitrophenol (DDNP), tetracene/lead trinitroresorcinate, lead trinitroresorcinate/KClO<sub>4</sub> and lead styphnate/KClO<sub>3</sub> may be used. Metal powder/KClO<sub>4</sub> is preferable by the considerations of thermal stability and good initiatability.

The metal powder may be a single or a combination of zirconium, tungsten, titanium, aluminum, magnesium, iron, nickel and copper. In view of good initiatability, a single zirconium or a mixture of zirconium and tungsten is preferable.

In a gas generator for air bag where such squib is held within a casing formed of a light metal material such as aluminum alloy, the gas generator for air bag comprising said squib having a layer structure consisting of an initiating agent contacted with the bridge wire and an spontaneous firing explosive composition contacted with said initiating agent, the spontaneous firing explosive composition being made of carbohydrates, oxyhalogenates, metal oxides and a synthetic resins, and a portion of the squib corresponding to the spontaneous firing explosive composition being exposed within said casing in a no good contact condition with said casing. More specifically, essentials of the squib formed of the above mentioned spontaneous firing explosive composition containing the synthetic resins are not required to be contacted well with the casing so as to improve the heat conductivity between the casing. Accordingly, an attachment structure for the squib to the casing can be simplified.

In addition, the casing of gas generator is made of a light metal material such as aluminum alloy, which is formed with an upper casing member and a lower casing member having an inner cylinder and an outer cylinder respectively, which are opposed to and frictional welded with each other corresponding to said inner cylinders and outer cylinders each other, and then a center space within said inner cylinder and an outer space surrounded by said inner cylinder and said outer cylinder are made. The present invention of a gas generator has a squib of which surface coated with an electrically insulating material, being inserted into said casing and fixed thereto, and the spontaneous firing explosive composition consisting of carbohydrates, oxyhalogenates, metal oxides and a synthetic resins being contained in the squib. Even when the heat conductivity to the squib is restricted by the electrically insulating material, the spontaneous firing function is not deteriorated. When said squib is inserted into a cylindrical-shaped boss projected from said casing into said center space and fixed thereto, it is preferable that said cylindrical-shaped boss is larger in height than the portion of said friction welding to avoid thermal effects on the squib upon welding.

The squib, the igniting agents and the gas generant in the gas generator for air bag are all have their own unique firing functions. The gas generator is subjected to a high temperature environments during summer or the like, and is mounted on a vehicle for a long time of many years. Accordingly, a high-temperature stability without deteriorating the firing function is required, which the high-temperature stability can be achieved with the metal oxides in the above mentioned explosive composition. The above mentloned spontaneous firing explosive composition contained in either one of the squib, the igniting agent and the gas generant is fired by its spontaneous firing function before the mechanical strength of the casing of the gas generator is deteriorated significantly upon vehicle fire or a warehouse fire. This firing is similar to a normal igniting upon such as a collision, and breakage of the casing is thus avoided. This spontaneous firing function can be kept by the metal oxides in the above mentioned spontaneous firing explosive composition even when being subjected to a high temperature environments during summer for many years. More specifically, a state where carbohydrates and oxyhalogenates are separated stably is ensured by the metal oxides, and then carbohydrates melts at a predetermined spontaneous firing temperature and reaches the oxohalogenates for firing.

When the above mentioned spontaneous firing explosive composition is contained in the squib, the Igniting agents or the gas generant, at first an exterior heat is transferred from outside to the squib, the igniting agent or the gas generant and then said explosive composition to be heated. Because of such indirect heating, the exterior heat may be less transferred depending on environments of the above mentioned explosive composition. In such a case, carbohydrates and oxyhalogenates are stably separated by the metal oxides while a state of carbohydrates's melt is not stable. So that, a straggling in spontaneous firing temperature is made. A synthetic resins serves to reduce the straggling and in turn to reduce the spontaneous firing temperature. The synthetic resins forms an adequate bridge among carbohydrates, oxyhalogenates and metal oxides. The carbohydrates is molten stably by heat conductivity via this bridge and reaches the oxyhalogenates passing through the metal oxides and the synthetic resins, so that spontaneous firing is caused. To ensure such phenomenon, it is desirable that the metal oxides has a predetermined particle diameter and contained at a predetermined amount, and that the synthetic resins is also contained at a predetermined amount. However, the synthetic resins may be omitted when the heat conductivity to the spontaneous firing explosive composition can be considered well.

20

50

### EP 0 665 138 A2

### BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 is a sectional view of a gas generator for air bag according to the present invention;
- Fig. 2 is a sectional view of a gas generator for air bag according to the present invention;
- Fig. 3 is a sectional view of a squib containing a spontaneous firing explosive composition according to the present invention;
  - Fig. 4 is a sectional view of a squib containing a spontaneous firing explosive composition according to the present invention;
  - Fig. 5 is a sectional view of a squib containing a spontaneous firing explosive composition according to the present invention;
    - Fig. 6 is a perspective view of a gas generant container;
    - Fig. 7 is a sectional view of a gas generant container, in which pellets of a gas generant of a spontaneous firing explosive composition according to the present invent ion are contained;
  - Fig. 8 is a sectional view of a gas generant container, in which powder of a gas generant of a spontaneous firing explosive composition according to the present invention is contained;
  - Fig. 9 is a sectional view of a igniting agents container, in which an igniting agents of a spontaneous firing explosive composition according to the present invention is contained;
  - Fig. 10 is a sectional view of an igniting agents container, in which a firing agents of a spontaneous firing explosive composition according to the present invention is contained;
  - Fig. 11 is a view illustrating a squib containing a spontaneous firing explosive composition according to the present invention being attached to an pressure tester; and
  - Fig. 12 is a view illustrating a squib containing a spontaneous firing explosive composition according to the present invention being attached to an initiating tester.

## 25 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS:

An example of a gas generator is described with reference to the drawing, in which the above mentioned squib, igniting agents and gas generant are contained. While one of the squib and the igniting agents may be omitted, the following description is made in conjunction with a case where both of them are contained. Fig. 1 shows a sectional view of a gas generator 60 for air bag according to the present invention.

in the gas generator 60 for air bag in Fig. 1, a reference numeral 27 represents a lower casing made of an aluminum alloy which comprises an inner cylinder 27a and an outer cylinder 27b. A reference numeral 28 represents an upper casing also made of an aluminum alloy which comprises an inner cylinder 28a and an outer cylinder 28b. The inner cylinder 27a and the outer cylinder 27b are respectively opposed to the inner cylinder 28a and the outer cylinder 28b and joined by friction welding between A and B portions to form a casing. In addition, a sack-shaped projecting portion 27c is integrally formed with the lower casing 27 at a center thereof. A communication hole 27d is provided in the projecting portion 27c at a center thereof. Further, orifices 33 are opened in the inner cylinder 28a of the upper casing 28. Diffusers 36 are opened in the outer cylinder 28b of the upper casing 28.

As mentioned above, the casing comprises an circular outer space 35 surrounded by the outer cylinder 27b of the lower casing 27 and the outer cylinder 28b of the upper casing 28 and a center space 34 defined by a portion surrounded by the inner cylinder 27a of the lower casing 27 and the inner cylinder 28a of the upper casing 28 and inside of the projecting portion 27c. A Igniting agents container 40 is contained in a portion surrounded by the inner cylinder 27a of the lower casing 27 and the inner cylinder 28a of the upper casing 28 in the center space 34. A squib 10 is contained in a position of the projecting portion 27c in the center space 34. The outer space 35 is divided by an inner wall 31 having orifices 32. A gas generant container 50 is contained inside the inner wall 31 while a first coolant 25 located at outlets of the orifices 32, a second coolant 26 and a filter 30 sealed with a filter cover 29 are contained exterior of the inner wall 31.

In particular, the squib 10 in the projection portion 27c is covered with an electrically insulating material 21 such as an elastomer and fixed with a calking member 27e of the lower casing 27 through a ferrite cover 22, a first keep plate 23 and a second keep plate 24. When the squib 10 covered with the electrically insulating material 21, the electrically insulating material 21 serves as a heat insulating material too. Accordingly, exterior heat is mainly transferred to the squib 10 through a pair of lead pins 7 in case of vehicle fire or the like.

As shown in Fig. 1, to insert the squib 10 into the projecting portion 27c through the electrically insulating material 21, an accuracy of molding of the electrically insulating material 21 is required to a certain degree. With this respect, as in a gas generator 61 for air bag shown in Fig. 2, the sack-shaped

projecting portion is replaced by a cylinder-shaped boss 27f. Most of portions of the electrically insulating material 21 and the squib 10 are projected into a position surrounded by the inner cylinder 27a of the lower casing 27 and the inner cylinder 28a of the upper casing 28 to provide easier assembly. In such a case, a height of the cylinder-shaped boss 27f is higher by a distance H than the friction welded site A to avoid thermal effect on the electrically insulating material 21 due to scattering burn as welding with friction. In addition, a bottom of the squib 10 abuts on the igniting agents container 40 through the electrically insulating material 21.

A normal operation of these gas generator 60 and 61 for air bag is described. First, the explosive in the squlb 10 is initiated when a predetermined electrical current is flown in a bridge which is not shown in Fig. 1 through the lead pins 7. A bottom of the squib is broken and then high-temperature and high-pressure gas is discharged. This high-temperature gas breaks the ligniting agents container 40 to cause the igniting agents contained therein to be fired. A high-temperature gas is generated as a result of burning of the igniting agents and passes through the orifices 33 and breaks the gas generant container 50 to cause the gas generant 51 contained therein to be ignited. A large amount of gas is generated as a result of burning of the gas generant 51. The generated gas passes through the orifices 32, the first coolant 25 and the second coolant 26 where cooling and collection of residues are made, then passes through the filter 30 where mists are removed and is discharged into an air bag which is not shown through the diffusers 36.

Fig. 3 shows an example where an initiating agents 4 and an spontaneous firing explosive composition 5 according to the present invention are aligned into a double layer structure within a magazine 8 of the squib 10. When the squib 10 is held in a manner as shown in Fig. 1, a portion of the squib 10 corresponding to the spontaneous firing explosive composition 5 is contained in the sack-shaped projecting portion 27c of the lower casing 27 with being coated with the electrically insulating material 21 which also serves as a heat insulating material. Fig. 4 shows an example where only the spontaneous firing explosive composition 5 according to the present invention is contained in the magazine 8 of a squib 11. Fig. 5 shows an example where an explosive bullet as the initiating agents 4 for a squib 12 and covered with the spontaneous firing explosive composition 5 according to the present invention is contained in the magazine 8 of a squib 12.

Normal operations of the squibs 10 and 12 shown respectively in Figs. 3 and 5 are as follows: first, when a predetermined electrical current is flown through electrode lead pins 7, the bridge 2 is heated, which causes the initiating agents 4 to be fired. Next, the explosive composition 5 is fired. The bottom of the squib is broken as the inside of the squib becomes high temperature and high pressure. As a result, a high-temperature, high-pressure gas is discharged. When the squib 10 or 12 is heated from outside due to, for example, an accident, the spontaneous firing explosive composition 5 is spontaneously fired at the time when the temperature within the squib reaches 165-220 °C or 165-200 °C. Next, the initiating agents 4 is fired. The end bottom of the squib is broken as the inside of the squib becomes high temperature and high pressure As a result, a high-temperature, high-pressure gas is discharged. Then, as described in conjunction with Figs. 1 and 2, the igniting agent container 40 is broken and then the gas generant container 50 is broken. The high-temperature, high-pressure gas is thus successively generated.

A normal operation of the squib 11 shown in Fig. 4 is as follows: first, when a predetermined electrical current is flown through the electrode lead pins 7, the bridge 2 is heated, which causes the explosive composition 5 to be iginited. The bottom of the squib is broken as the inside of the squib becomes high temperature and high pressure. As a result, a high-temperature and high-pressure gas is discharged. When the squib 11 is heated from outside and then the temperature within the squib reaches 165-220 °C or 165-200 °C, the spontaneous firing explosive composition 5 is spontaneously fired at the time. The bottom of the squib is broken as the inside of the squib becomes high temperature and high pressure. As a result, a high-temperature and high-pressure gas is discharged. Then, as described in conjunction with Figs. 1 and 2, the igniting agents container 40 is broken and then the gas generant container 50 is broken. The high-temperature and high-pressure gas is thus successively generated.

As mentioned above, the spontaneous firing explosive composition in Figs. 3 through 5 is spontaneously fired at 165-220 °C or 165-200 °C. Accordingly, when the casings 27 and 28 in Figs. 1 and 2 is made of a light aluminum alloy, the spontaneous firing explosive composition is to be fired before the mechanical strength is deteriorated as the casing is heated due to firing or the like. Thus, there is no fear of breakage of the casing or scattering of broken pieces. In particular, when the spontaneous firing explosive composition according to the present invention is contained in the igniting agents container 40 or the gas generant container 50 in Figs. 1 and 2, the squib may be left without firing. On the contrary, when the spontaneous firing explosive composition according to the present invention is contained in the squib, all explosive in the gas generator is fired.

In particular, as shown in Figs. 1 and 2, when the heat conductivity to the squib 10 is restricted by the electrically insulating material 21 or a projection from the container, it is preferable that the spontaneous firing explosive composition is included a synthetic resins. In this case, the spontaneous firing explosive composition consists of carbohydrates, oxyhalogenates, metal oxides, a synthetic resins, and is to be fired stably at a low temperatures of 165-220 °C.

Fig. 6 shows an example of an appearance of the gas generant container 50. The gas generant is contained in a container formed of a cup of aluminum foll.

Fig. 7 shows an example of a sectional view where the spontaneous firing explosive composition according to the present invention is contained in the gas generant container 50 as the gas generant 51 of pellets shape. Fig. 8 shows an example of a sectional view where the spontaneous firing explosive composition according to the present invention is contained in the gas generant container 50 as the gas generant 51 of powder. In Figs. 7 and 8, a reference numeral 52 represents a ceramic cushion material for use in avoiding oscillation and vibration of the gas generant.

In Fig. 1, In case of the gas generator 60 having this gas generant container 50 of which a gas generant is the spontaneous firing explosive composition 5 according to the present invention, and when the gas generant container 50 is heated from outside due to vehicle firing or warehouse firing and then a temperature of the gas generant (spontaneous firing explosive composition) 51 contained in the gas generant container 50 reaches 165-220 °C or 165-200 °C, the gas generant (spontaneous firing explosive composition) 51 is spontaneously fired and breaks the gas generant container 50. A high-temperature gas passes through the orifices 33 and breaks the igniting agents container 40 to fire the igniting agents. At the same time, it is passed through the first coolant 25 and the second coolant 26, and is then discharged outward through the filter 30. The gas generant (spontaneous firing explosive composition) 51 in Fig. 7 or 8 is spontaneously fired at 165-220 °C or 165-200 °C, so that there is no fear of breakage of the casing and scattering of the broken pieces even if the lower casing 27 and the upper casing 28 in Fig. 1 is made of light aluminum alloy.

Fig. 9 shows an example where the spontaneous firing explosive composition 5 according to the present invention is contained in the igniting agents container 40. Fig. 10 shows an example where the spontaneous firing explosive composition 5 according to the present invention is contained in the igniting agents container 40 along with the igniting agents 41 made of boron/potassium nitrate with a two-layer structure.

In Fig. 1, in case of the gas generator 60 having this igniting agents container 40 heated from outside due to vehicle firing or warehouse firing, and then a temperature of the spontaneous firing explosive composition 5 contained in the igniting agents container 40 reaches 165-220 °C or 165-200 °C, the spontaneous firing explosive composition 5 is spontaneously fired and breaks the igniting agents container 40. This discharges a high-temperature and high-pressure gas. The discharged gas passes through the orifices 33 and breaks the gas generant container 50 to fire the gas generant 51 contained therein. A large volume of gas is generated as a result of burning of the gas generant 51. The generated gas is passed through the first coolant 25 and the second coolant 26, and is then discharged outward through the filter 30. The spontaneous firing explosive composition 5 in Fig. 9 or 10 is spontaneously fired at 165-220 °C or 165-200 °C, so that there is no fear of breakage of the casing and scattering of the broken pieces even if the lower casing 27 and the upper casing 28 in Fig. 1 is made of light aluminum alloy.

Properties of the present invention of the spontaneous firing explosive composition are not deteriorated during a heat aging test at 120 °C for 100 hours or 107 °C for 400 hours, which are considered to be the most of severe environments that might be caused in vehicles or the like in a normal usage. In addition, it can maintain the spontaneous firing function and other inherent ignition functions. Here are explained in conjunction with the following examples.

Now, the present invention is described specifically in conjunction with a specific sets of examples and comparative examples. The present invention is not limited to those examples. First, illustrated are examples where a squib contained a spontaneous firing explosive composition (carbohyd rates/oxyhalogenates/metal oxides) according to the present invention comprising no synthetic resins. This squib was assessed solely, too. A term "part" used in the examples represents a part by weight.

## Examples 1 through 3, Comparative Examples 1 through 3

In Fig. 11, a pressure sensor 110 was attached to a SUS container 100 with a space 101 of a capacity of 10 milli-liters. The squib 10 was attached to a lid of the SUS container 100. The electrode lead pins 7 of the squib 10 were connected to a squib ignition power source and an oscillograph for current measurement. A terminal of the pressure sensor 110 was connected to the measurement oscillograph. A predeter-

mined electrical current was flown across the squib to ignite it. An initiating time t (msec.) and a maximum generated pressure value Pmax. (psi) were measured. An initiating time t in Table 1 means a time interval from time when electrical current has finished flowing through the squib to time of starting raising the pressure.

A spontaneous firing explosive composition was prepared as follows, 1.2 parts of super fine powder of light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.001 mm or smaller was added to and mixed with 74.8 parts of potassium chlorate (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.2 mm. After mixing, it was found that the magnesium oxide was coated on the surfaces of the potassium chlorate when observed through an optical microscope, Next, 1.0 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 23.0 parts of sucrose (Taito Corporation) having an average particle diameter of 0.05 mm. After mixing, it was found that the surfaces of the sucrose was coated with the magnesium oxide when observed through an optical microscope. The above mentioned total amount of potassium chlorate/magnesium oxide and sucrose/magnesium oxide were mixed with each other to obtain the spontaneous firing explosive composition.

The squib was assembled in a following manner. A squib sheath 9 was placed in the squib cup 6 as shown in Fig. 3, in which 40 mg of the spontaneous firing explosive composition 5 was added. Subsequently, 120 mg of the initiating agents 4 (zirconium/potassium perchlorate) were placed and a squib sealing plug 1 was engaged therewith. For comparison, a explosive of sucrose/potassium chlorate with no magnesium oxide added. In addition, a squib was assembled in the same manner as those described above. Histories of the squibs were following three of types: the room temperature only, 120 °C  $\times$  100 hours and 107 °C  $\times$  400 hours. The results are given in Table 1. For comparative examples, the explosives were non-initiating in both 120 °C  $\times$  100 hours and 107 °C  $\times$  400 hours. On the contrary, no change in pressure was found for those according to the present invention.

# Examples 4 through 6, Comparative Examples 4 through 6

In Fig. 12, the squib 10 was attached to a lid of a SUS container 120 having a space 101 of a capacity of 10 milli-liters. A hole for temperature measurement was formed in the lid, in which a thermocouple was inserted to monitor temperature in the container. The container 120 was heated with a Bunsen burner. The container temperature at which the squib was spontaneously fired were recorded. The squib was as same as that used in the above mentioned examples. The results are given in Table 2. For comparative examples, the explosives were misfired in both  $120\,^{\circ}$ C  $\times$  100 hours and 107  $\,^{\circ}$ C  $\times$  400 hours. On the contrary, those according to the present invention were all fired spontaneously at and around 200  $\,^{\circ}$ C after the above mentioned heat aging tests.

## Examples 7 through 9, Comparative Examples 7 through 9

In Fig. 1, the same squib as the one described in said examples was attached to a gas generator of an aluminum casing where the amount of the gas generant pellets 51 and the igniting agents 41 were respectively 55 gram and 1.7 gram. The gas generator was suspended in the air and subjected to a bonfire test with being heated by flame generated by firewood to be spontaneously fired. A heating time until spontaneous firing and a state of the gas generator after firing were observed. The results are given in Table 3. For comparative examples, the heat aging tests of 120 °C × 100 hours and 107 °C × 400 hours both resulted in casing breakage. On the contrary, those according to the present invention were approximately similar to the state of the room temperature.

50

25

non-initiate

absence

0

Examples

12001

Comparative

non-initiate

absence

107c

rated pressure 190 280 Pmax (psi.) 2502 1 0 5 ij <u>...</u>; initiating time 10 Effect of MgO on Squib temperature history (1) 10 t (msec) ıO ත <del>,</del> i 0 ٠; -Squib initiating test-15 composition MgO presence presence explosive presence absence 20 Squib temperature 4 0 0 hours history of temperature 100 hours temperature 1075 120C 25 T00B F00# 30 ટ્ર --2 3 [TABLE 1 ] Examples

50

45

35

40

EP 0 665 138 A2

Effect of MgO on Squib temperature history (2) -Squib spontameous firing test-

comments					stop heating at container temperature of 300°C	stop heating at container temperature of 300°C
heating time	2min. 40sec.	2min. 50sec.	2min. 45sec.	2min. 23sec.		
container temperature upon firing t	203	210	208	188	misfire	misfire
explosive composition MgO	presence	presence	presence	absence	absence	absence
history of explosive Squib temperature composition MgO	room temperature	120°C 100 hours	1075 400 hours	room temperature	120°C 100 hours	107°C 400 hours
2	4	r.	9	4	വ	မ
		Examples			Comparative Examples	•

[TABLE 2]

5	3)	Appearance of gas gen- erator after firing	No-trouble	No-trouble	No-trouble	No-trouble	casing breakage	casing breakage
15	re history (	heating time	2 5 sec.	2min, 38sec.	2ain, 33sec.	2min. 17sec.	5ain. O3sec.	4min. 38sec.
20	Effect of MgG on Squib temperature history (3) -Bonfire test~	explosive composition MgO	presence	presence	presence	absence	absence	absence
25	Effect of MgD o	history of Squib temperature	room temperature	120℃ 100 hours	107°C 400 hours	room temperature	120°C 100 hours	107t 400 hours
30		No	-	- ∞	6	t-	∞	6
35	[TABLE 3]			Examples			Comparative Examples	

Next, illustrated are examples where a spontaneous firing explosive composition (carbohydrates/oxyhalogenates/metal oxides based) according to the present invention contained in the gas generant.

## Examples 10 through 18, 19 through 21

45

An spontaneous firing explosive composition was prepared as follows. 1.2 parts of super fine powder of light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.001 mm or smaller was added to and mixed with 74.8 parts of potassium chlorate (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.2 mm. After mixing, it was found that the surfaces of the potassium chlorate was coated with the magnesium oxide when observed through an optical microscope. Next, 1.0 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) were added to and mixed with 23.0 parts of sucrose (Taito Corporation) having an average particle diameter of 0.05 mm. After mixing, it was found that the surfaces of the sucrose was coated with the magnesium oxide when observed through an optical microscope. The above mentioned total amount of potassium chlorate/magnesium oxide and sucrose/magnesium oxide were mixed with each other to obtain the spontaneous firing explosive composition.

This spontaneous firing explosive composition was placed in a milt of which diameter is 10 mm and press-molded under a load of 500 kilo-gram. And then pellets of the gas generant were obtained. Its weight of one pellet is approximately 0.6 gram. As shown in Fig. 7, the above mentioned pellets 30 gram were

35

40

45

50

55

#### EP 0 665 138 A2

placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are: room temperature, 120 °C × 100 hours and 107 °C × 400 hours. We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the igniting agents container 40 having the igniting agents (boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 4 and Table 6. Differences in temperature histories during the 60-liter tank pressure-time test were slight. During the bonfire test, there were no differences in temperature histories found. An igniting time t in Table 4 is a time interval from time when electrical current has finished flowing through the squib to time of starting raising the pressure.

## Comparative Examples 10 through 18, 19 through 21

For comparison with the above mentioned examples, the gas generant was made of a sucrose/potassium chlorate without adding magnesium oxide. As in the above, the gas generant without magnesium oxide was placed in a mill of which the diameter is 10 mm and press-molded under a load of 500 kilo-gram. And then peliets of the gas generant were obtained. Its weight of one pellet is approximately 0.6 gram. As shown in Fig. 7, the above mentioned pellets 30 gram were placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are: room temperature, 120 °C x 100 hours and 107 °C x 400 hours. We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 mille-gram, the igniting agents container 40 having the igniting agents (boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 5 and Table 6. During the 60-liter tank pressure-time test, no gas generant was ignited with the temperature histories of 120 °C x 100 hours and 107 °C x 400 hours. During the bonfire test, gas generation were made abnormally with the temperature histories of 120 °C x 100 hours and 107 °C x 400 hours.

55

EP 0 665 138 A2

	Г	t		r	····				T	T	-
5		abnormal appearance	none	none	none	none	none	none	none	попе	none
70		maximum pressure time(msec)	58.3	55.7	66.4	57.5	53.8	69. 7	60.2	55.4	65.3
	ets(1)	maximum pressure KPa	223.3	288.1	170.2	219.4	277.0	176.6	230.2	266.1	165.8
15	generant pelle	igniting time t (msec)	6.6	6.0	8.8	7. 2	5.9	9. 2	7.8	6. 5	es
20 25	rature history of gas   60-liter tank test	gas generator test temperature	room temperature	852	-40t	room temperature	855	-40c	room temperature	850	-40c
30	Bffect of MgO on temperature history of gas generant pellets(1) 60-liter tank test	presence or absence of MgO		presence	<u> </u>		presence	<b>!</b>		presence	
35	Bffect of	temperature history of gas generant		room temperature			120c 100 hours			1075 400 hours	
40		Š	22	11	12	13	14	15	16	17	82
45	[TABLE 4]					W. Carlo	Examples				

EP 0 665 138 A2

		en en			1			1			$\overline{}$
5		abnormal appearance	none	none	none						
		waxinum pressure time(msec)	51.1	49.3	59. 1						
10	ts (2)	maximum pressure KPa	240.5	299.9	200.8					-	
15	generant pelle	igniting time t (msec)	6.0	5. 5	8. 4	non-ignite	non-ignite	non∼ignite	non-ignite	non-ignite	non-ignite
20 25	rature history of gas   60-liter tank test	gas generator test temperature	room temperature	258	-40c	room temperature	850	-40¢	room temperature	850	-40c
30	Effect of MgD on temperature history of gas generant pellets(2) 60-liter tank test	presence or absence of MgO		absence			absence			absence	
35	Bffect of	temperature history of gas generant	7	temperature		\$	100 hours		, t	400 hours	
40		No.	10	11	12	£1	14	15	91	17	≈ ≃
<b>4</b> 5	KTABLE 5 1						Comparative	txamples		•	

55

35	30	25	15 20	10	5
CTABLE 6 1	Effect	Effect of MgO on temperature history of gas generant pellets(3) -Bonfire test-	ure history of gas -Bonfire test-	generant pelle	.ts (3)
	8	temperature history of gas generant	presence or absence of MgO	heating time	Appearance of gas generator after firing
	19	room temperature	presence	2min. 3 5 sec.	No-trouble
Examples	8	120°C 100 hours	presence	2min, 5 1 sec.	No-trouble
	21	107°C 400 hours	presence	. 2min. 38sec.	No-trouble
	61	room temperature	absence	2πin. 13sec.	No-trouble
Comparative Examples	08	120°C 100 hours	absence	4 min. 3 9 sec.	misfire gas generants
	21	107°C 400 hours	absence	5min, 12sec,	misfire gas generants

### Examples 22 through 30, 31 through 33

40

An spontaneous firing explosive composition was prepared as follows. 23.0 parts of wood powder having an average particle diameter of 0.05 mm was added to and mixed with 1.0 parts of said light magnesium oxide(reagent; Wako Pure Chemical Industries Co., Ltd.), to which 76.0 parts of potassium chlorate/magnesium oxide mixture prepared in said examples was added and mixed with each other. 24.0 parts of the above mentioned wood powder/potassium chlorate/magnesium oxide composition was mixed with 76.0 parts of spontaneous firing explosive composition based on sucrose/potassium chlorate/magnesium oxide prepared in said examples to obtain gas generant in the form of powder. As shown in Fig. 8, the above mentioned gas generant 30 gram was placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are : room temperature, 120 °C x 100 hours and 107 °C x 400 hours. We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the igniting agent container 40 having the igniting agent (boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 7 and Table 9. Differences in temperature histories during the 60-liter tank pressure-time test were slight. During the bonfire test, there were no differences in temperature histories found.

## Comparative Examples 22 through 30, 31 through 33

The gas generant was made of a wood powder/sucrose/potassium chlorate mixture without adding magnesium oxide by the same manner in the above mentioned examples 22 to 30. As shown in Fig. 8, the above mentioned gas generant 30 gram was placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are : room temperature,  $120 \, ^{\circ}\text{C} \times 100$  hours and  $107 \, ^{\circ}\text{C} \times 400$  hours. We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the alumInum casing was assembled. The gas generator 60 contains the squib 10 having zirco-nlum/potassium perchlorate 120 milli-gram, the igniting agents container 40 having the igniting agents-(boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 8 and Table 9. During the 60-liter tank pressure-time test, no gas generant was ignited with the temperature histories of  $120 \, ^{\circ}\text{C} \times 100$  hours and  $107 \, ^{\circ}\text{C} \times 400$  hours. During the bonfire test, gas generation were made abnormally with the temperature histories of  $120 \, ^{\circ}\text{C} \times 100$  hours and  $107 \, ^{\circ}\text{C} \times 400$  hours.

55

EP 0 665 138 A2

		abnormal appearance	none	none	none	попе	попе	попе	none	none	пове
5					_						
10		maximum pressure tine (msec)	60.9	51.3	70.3	63.8	61.0	73.9	59. 4	52.0	75.5
15	vder (1)	maximum pressure KPa	235.2	271.1	160.4	240.0	281.3	176.5	226.6	267.2	180.
	generant pow	igniting time t (msec)	5. 5	4.9	7. 2	5.3	5. 1	6.6	4.8	4.9	7. 0
20 25	rature history of gas —60-liter tank test—	gas generator test temperature	room temperature	855	-40¢	room temperature	358	-40¢	room temperature	855	-40c
30	Effect of MgO on temperature history of gas generant powder(1) —60-liter tank test—	presence or absence of MgO		presence			presence	1		presence	
35	Bffect of	temperature history of gas generant		temperature			120C			10fC 400 hours	
40		8	22	ಚ	24	25	92	22	88	53	8
<del>4</del> 5	TABLE 7 3						Examples			•	

EP 0 665 138 A2

	ſ	12 gg				<u> </u>					
5		abnormal appearance	none	none	лопе						1
		maximum pressure time(msec)	58.8	53.4	70.3						
10	ır (2)	maximum pressure KPa	240.5	288. 1	190.3		-	1			
15	generant powde	igniting time t (msec)	5. 3	4.5	8.0	non-ignite	non-ignite	non-ignite	non-ignite	non-ignite	non-ignite
20 25	rature history of gas -60-liter tank test	gas generator test temperature	room temperature	850	-40c	room temperature	328	-40c	room temperature	855	-40£
30	Effect of MgO on temperature history of gas generant powder(2) 	presence or absence of MgO		absence			absence			absence	
35	Effect of	temperature history of gas generant		room temperature			120C 100 hours			1075 400 hours	
40		ક	22	ĸ	24	25	92	27	88	ह्य	8
45	[TABLE 8 ]						Comparative	Examples		•	

5	иder (3)	Appearance of gas generator after firing	No-trouble	No-trouble	No-trouble	No-trouble	misfire gas generant	misfire gas generant
10	as generant poo	heating time	2min, 43sec,	2min. 47sec.	2min. 33sec.	2min. 28sec.	5 min. O 2 sec.	4min. 51sec.
20	iture history of g -Bonfire test-	presence or absence of MgO	presence	presence	presence	absence	absence	absence
25	Bffect of MgO on temperature history of gas generant powder(3) -Bonfire test-	temperature history of gas generant	room temperature	120°C 100 hours	107°C 400 hours	room temperature	120°C 100 hours	107t 400 hours
30	Bffe	No	31	32	33	19	20	21
35	[TABLE 9 ]			Examples			Comparative Examples	

Next, illustrated are examples where a spontaneous firing explosive composition (carbohyorder drates/oxyhalogenates/metal oxides) according to the present invention was contained in the igniting agents
41

## Examples 34 through 42, 43 through 45

A spontaneous firing explosive composition was prepared as follows. 1.2 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 74.8 parts of potassium chlorate oxide(reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.2 mm. After mixing, it was found that the surfaces of the potassium chlorate was coated with the magnesium oxide when observed through an optical microscope. Next, 1.0 parts of said light magnesium (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 23.0 parts of sucrose (Taito Corporation) having an average particle diameter of 0.05 mm. After mixing, it was found that the surfaces of the sucrose was coated with the magnesium oxide when observed through an optical microscope. The above mentioned total amount of potassium chlorate/magnesium oxide and sucrose/magnesium oxide were mixed with each other to obtain the spontaneous firing explosive composition.

As shown in Fig. 9, the above mentioned explosive composition 1.0 gram was placed in the igniting agents container 40 and sealed. Twelve containers such as the above mentioned igniting agents containers 40 were ready. We applied three types of temperature histories. Here are: room temperature,  $120 \,^{\circ}\text{C} \times 100$  hours and  $107 \,^{\circ}\text{C} \times 400$  hours. We used four containers to each types, Thereafter, as shown in Fig. 1, the

35

40

45

50

55

### EP 0 665 138 A2

gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the gas generant container 50 having the gas generant 55 gram of based on sodium azide, and the Igniting agents container 40 having the above mentioned spontaneous firing explosive composition. This gas generator 60 was used for test of a pressuretime with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 10 and Table 12. Differences in temperature histories during the 60-liter tank pressure-time test were slight, During the bonfire test, there were no differences in temperature histories found. An igniting time t in Table 10 and Table 11 means a time interval from time when electrical current has finished flowing through the squib to time of starting raising the pressure. A heating time t in Table 12 means a time for the gas generator 60 to fire, Maximum pressure time means a time for pressure to become maximum.

## Comparative Examples 34 through 42, 43 through 45

For comparison with the above mentioned examples, igniting agents 41 were made of a sucrose/potassium chlorate without adding magnesium oxide, As in the above, the igniting agents 41 without magnesium oxide were placed in the igniting agents container 40 as in said examples. Twelve containers such as the above mentioned igniting agents containers 40 were ready, We applied three types of temperature histories, That is : room temperature, 120 °C x 100 hours and 107 °C x 400 hours. We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator of the same specifications as in said examples except for the igniting agents were assembled. This gas generator is used for conducting the same assessment tests as in said examples. The results are given in Table 11 and Table 12. During the 60-liter tank pressure-time test, the explosives were all non-ignited and the gas generant was failed to be ignored with the temperature histories of 120 °C  $\times$  100 hours and 107 °C  $\times$  400 hours. During the bonfire test, the casings were broken down with the temperature histories of 120 °C x 100 hours and 107 °C × 400 hours.

55

# EP 0 665 138 A2

		abnormal appearance	none	попе	none	попе	none	попе	none	none	none
5		abn	_								
		maximum pressure time (msec)	0	∞ .	. 4	0,	6.		es .	∞	4
10		maximum pressur time (ms	5 4.	4 2.	59:	52.	41	5 8.	53	4 0.	5.8
	y (1)	maximum pressure KPa	). 4	8.6	5.3	7. 2	5. 3	7. 7	9. 5	5. 2	8.8
15	histor	maximum pressur KPa	150.	178	13	14	17	13	14	17	1 3
	rature	gniting time t (msec)	0	∞.	. 3	∞ .	6	9 .	. 2	<del></del>	
20	tempe	igniting time t (msec)	.c.	3.	θ.	4.	3.	6.	5.	4.	9.
	agents k test	rator ture	ture	2,9	۵	ture	5 C	္	ıture	ည	p Q
25	Effect of MgO on igniting agents temperature history (1)	gas generator test temperature	room temperature	8 5	-40c	room temperature	8 5	-40¢	room temperature	850	-40c
2.0	on ig -60-1i		·	l	ļ		<u>i.,</u> .	L		l	1
	of MgO	presence or absence of MgO		presence			presence		į	presence	
30	<b>E</b> ffect	preser absenc		E.			E.			<b>E</b> .	
		sents		e i i e			ırs			ers.	
35		temperature history of igniting agents		room temperature			120C 100 hours			107c	
		tempe hista igni		ţ			1 (	·		. 4	
40		8	34	35	38	37	88	88	\$	41	42
	<b>L</b> 01						t) les				
4E	[TABLE 10]						Bxamples				!
45		<u>K</u>	L								

EP 0 665 138 A2

5		abnormal appeara- nce	none	none	попе				]	1	
10		maximum pressure time (msec)	53. B	40.7	60.3						
10	ory (2)	maximum pressure KPa	155.5	177. 4	129. 1				1.	1	1
15	perature histo	igniting time t (asec)	4.8	4.0	6. 1	non-igniting	non-igniting	non-igniting	non-igniting	non-igniting	non-igniting
20 25	on igniting agents tem —60-liter tank test—	gas generator test temperature	room temperature	850	-40¢	room temperature	352	-40¢	room temperature	352	-40¢
30	Bffect of MgO on igniting agents temperature history (2) 60-liter tank test	presence or absence of MgO		absence			absence			absence	
35	B	temperature history of igniting agents		temperature		,	100 hours		\$ C	400 hours	
40		ક્ર	34	33	36	37	38	33	8	41	42
45	KTABLE 113			-			Comparative	SOTOES SO		•	

5		Appearance of gas generator after firing	No-trouble	No-trouble	No-trouble	No-trouble	casing breakage	casing breakage
10	story (2)	Appean gas ge after	-0X	-05	No-	-ox	casin	casin
15	emperature hi	heating time	2 min. 3 5 sec.	2min. 44sec.	· 2 min. 5 O sec.	2 min. 2 8 sec.	4min. 52sec.	5min. O 1 sec.
20	igniting agents t Bonfire test-	presence or absence of MgO	presence	presence	presence	absence	absence	absence
25	Bffect of MgO on igniting agents temperature history (2) -Bonfire test-	temperature phistory of a igniting agents	room temperature	120℃ 100 hours	1075 400 hours	room temperature	120°	107°C 400 hours
30		ter No his ig	43	44	53	43	44	45
35	[TABLE 12]			Bxamples	,		Comparative Examples	

Next, described in conjunction with Table 13 are various exemplified combinations of carbohydrates and metal oxides in a three-component spontaneous firing explosive composition of carbohydrates/oxyhalogenates/metal oxides.

### Examples 46 through 48, Comparative Example 46 through 51

55

The combination given in Table 2 was mixed at the following ratio to prepare a explosive composition. Sucrose (Taito Corporation) 23.0% by weight (Example 46, Comparative Examples 46 and 47)

Dextrin (reagent; Kishida Chemical Industries Co., Ltd.) 23.0% by weight (Example 47, Comparative Examples 48 and 49)

Cellulose (reagent; Wako Pure Chemical Industries Co., Ltd.) 23.0% by weight (Example 48, Comparative Examples 50 and 51)

Potassium Chlorate (reagent; Kanto Chemical Co., Ltd.) 74.0% by weight (Examples 46 through 48) and 77.0% by weight (Comparative Examples 46 through 51)

MgO (reagent; Wako Pure Chemical Industries Co., Ltd.) 2.0% by weight (Example 46)

ZnO (reagent; Wako Pure Chemical Industries Co., Ltd.) 2.0% by weight (Example 47)

CaO (reagent; Wako Pure Chemical Industries Co., Ltd.) 2.0% by weight (Example 48)

The mixture was made by means of two steps mixing, wherein at first, carbohydrates and potassium chlorate were respectively mixed up with metal oxides, and then these mixtures were mixed together.

### EP 0 665 138 A2

The resultant spontaneous firing explosive compositions were subjected to measurements on the pressure maximum time and the generated pressure by using a test vessel obtained by attaching a pressure sensor to a stain less vessel having an inner volume of 1 liter, in which the spontaneous firing explosive composition 15 gram was burned in the form of powder (1-liter tank test).

To ignite the spontaneous firing explosive composition, an ignitor having firing agents 0.6 gram contained of a boron/potassium nitrate and lead styphnate fuse heads were used. The pressure maximum time means a time interval from time when electrical current has finished flowing through the ignitor to time of raising the pressure till maximum.

The spontaneous firing explosive compositions were applied with temperature histories of  $120 \,^{\circ}\text{C} \times 100$  hours and  $107 \,^{\circ}\text{C} \times 400$  hours to determine the heat aging properties. A spontaneous firing temperature of the spontaneous firing explosive composition was measured by using a differential scanning calorimetry (Type DSC 220: Selko Instruments Inc.). The results of the above test are summarized in Table 13.

### EP 0 665 138 A2

KTABLE 131												
				components			ini	initial properties	erties	propert	properties after 100 hours	100 hours
		carbohydrates	drates	potassium	metal	metal oxides						200
_			0000	-		on change	maximum		spontaneous	maximum	max imum	Spontaneous
/	ž	type	particle diameter	e average r particle	type	particle diameter	time	o to coo to	<del></del>	time		temperature
<i></i>		4	(mm)	ē		(mm)	(msec)	(atm)	(£)	(asec)	(atm)	(£)
	46	sucrose	0.02	0.2	OBW	≤0.001	43	40.5	188	44	39.0	193
	47	dextrin	0.01	0.1	SnO	0.03	5.1	34.2	220	23	3,0, 1	23.1
Syd III Dyd	48	powder cellulose	0.03	3 0.1	CaO	0.01	57	29.9	248	62	27.3	255
	46	sucrose	0.6	0.2	absence		4.2	41.7	183	no-ignite		
	47	sucrose	0,02	2 0 2	absence		2.0	3.7.0	172	no-ignite		
1	\$	dextrin	0.7	0.1	absence		53	32.1	223	no-ignite		
Examples	49	dextrin	0.01	0.1	absence		49	32.8	210	no-ignite		
	50	powder cellulose	0.03	3 0.1	absence		5 3	27.6	243	no-igníte		
	51	powder celiulose	0.03	3 0.1	absence		5 5	30.4	242	no-ignite		

In Examples 46 through 48, there was no significant difference in properties between the initial properties and those after heat aging at 120 °C for 100 hours because the conditions met the specifications according to the present invention.

In Comparative Examples 46 through 51, non-igniting were found in all after the heat aging at 120 °C for 100 hours because there were no metal oxides contained. In addition, the spontaneous firing tempera-

### EP 0 665 138 A2

ture couldn't be measured. For the state after heat aging, no changes were found in Examples while their color of test vessel change into black-brown due to effect of heat in all Comparative Examples .

As apparent from the above, the spontaneous firing explosive composition according to the present invention has a spontaneous firing function in a specific high-temperature range and kept a stable burning capability after the heat aging at 120 °C for 100 hours.

Next, described are examples where a four-component spontaneous firing explosive composition according to the present invention (carbohydrates/oxyhalogenates/metal oxides/synthetic resins) is contained in the squib. This squib was assessed solely, too.

## Examples 1 through 3, Comparative Examples 1 through 3

In Fig. 11, a pressure sensor 110 was attached to a SUS container 100 with a space 101 of a capacity of 10 milli-liters. The squib 10 was attached to a lid of the SUS container 100. The electrode lead pins 7 of the squib 10 were connected to a squib ignition power source and an oscillograph for current measurement.

A terminal of the pressure sensor 110 was connected to the measurement oscillograph. A predetermined electrical current was flown across the squib to initiate it. An initiating time t (msec.) and maximum pressure value Pmax. (psi.) were measured. An initiating time t (msec.) means a time up to start raising the pressure after an electrical current has finished flowing through the squib.

A spontaneous firing explosive composition was prepared as follows. 1.2 parts of said super fine powder of light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 74.8 parts of potassium chlorate (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.2 mm, After mixing, it was found that the surfaces of the potassium chlorate was coated with the magnesium oxide when observed through an optical microscope. Next, 1.0 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 23.0 parts of sucrose (Taito Corporation) having an average particle diameter of 0.05 mm. After mixing, it was found that the surfaces of the sucrose was coated with the magnesium oxide when observed through an optical microscope. The above mentioned total amount of potassium chlorate/magnesium oxide and sucrose/magnesium oxide were mixed with each other, to which 5.0 parts of silicon resin (Shin-etsu Silicon KE 441T; Shin-etsu Chemical Co., Ltd.) was added. The mixture was kneaded over 30 minutes. Thereafter, the mixture was stood at a room temperature over 48 hours to cure the silicon resin, thereby to obtain the spontaneous firing explosive composition.

The squib was assembled in a following manner. A squib sheath 9 was placed in the squib cup 6, in which the spontaneous firing explosive composition 60 milli-gram was added. Subsequently, the initiating agents 4 (zirconium/potassium perchlorate) 140 milli-gram was placed and a squib sealing plug 1 was engaged therewith. For comparison, an explosive made of sucrose/potassium chlorate/magnesium oxide with no synthetic resins, in addition, the squib was assembled in the same manner as those described above. Histories of the squib temperature were following three types: the room temperature only,  $120 \,^{\circ}$ C × 100 hours and 107  $\,^{\circ}$ C × 400 hours, The results are given in Table 14, there were significant straggling on comparative examples of both 120  $\,^{\circ}$ C × 100 hours and 107  $\,^{\circ}$ C × 400 hours, On the contrary, those according to the present invention provided stable results in the initiating time as well as the generated pressure.

## Examples 4 through 6, Comparative Examples 4 through 6

In Fig. 12, the squib 10 was attached to a lid of a SUS container 120 having a space 101 of which a capacity is 10 milli-liters. A hole for temperature measurement was formed in the lid, in which a thermocouple was inserted to monitor a temperature in the container. The container 120 was heated with a Bunsen burner. The container temperature at which the spontaneous firing explosive composition in the squib was spontaneously fired was recorded. The squib was as same as that used in the above mentioned examples. The results are given in Table 15. On comparative examples, the spontaneous firing explosive composition in the squib were spontaneously fired at 200 °C or higher, and of which struggling were significant. On the contrary, those according to the present invention were all spontaneously fired at and around 180 °C after the above mentioned heat aging test with less straggling.

## Examples 7 through 9, Comparative Examples 7 through 9

In the gas generator 61 for air bag in Fig. 2 where the squib 10 was exposed to within the casing, the same squib as the one described in said examples was attached to a gas generator of an aluminum casing

55

### EP 0 665 138 A2

where the amount of agents in the gas generant pellets 51 and the igniting agent 41 were 55 gram and 1.7 gram, respectively. The gas generator was suspended in the air and subjected to a bonfire test with being heated by flame generated by firewood to be spontaneously fired. A heating time until spontaneous firing and a state of the gas generator after firing were observed. The results are given in Table 16. On comparative examples, the heat aging tests of  $120\,^{\circ}$  C  $\times$  100 hours and 107  $^{\circ}$  C  $\times$  400 hours both resulted in filter breakage. On the contrary, those according to the present invention were not changed in appearance.

	Γ			i i			1	
	Œ	maximum pressure Pmax (psi,)	1,650	1, 610	1, 620	1,670	1, 480	1.520
,	erature history	initiating time t (msec)	1.11	1, 12	1. 12	1. 10	1.05	1.08
5	ic resins on Squib tempe -Squib initiating test-	presence or absence of synthetic resins	presence	présence	presence	absence	absence	absence
36 35	Bffect of synthetic resins on Squib temperature history (1) -Squib initiating test-	temperature history of Squib	room temperature	120°C 100 hours	107°C 400 hours	room temperature	120°C 100 hours	107c 400 hours
	Ħ	No.		2	က	7	2	ന
40	[TABLE 14]			Bxamples			Comparative Examples	
45								

EP 0 665 138 A2

5 comments 10 Bffect of synthetic resins on Squib temperature history (2) heating 2min. 03sec. 2min. 35sec 2min, 2 min. 2min, 4 6 sec. 2min. 1 0 sec. 0 7 sec. 5 1 sec. t ine 15 container temperature -Squib spontaneous firing testupon firing 20 1 7 8 180 202 2 1 2 214 181 9 25 synthetic resins presence or presence absence of presence presence absence absence absence 30 35 temperature 1 0 0 hours temperature 1 0 0 hours 4 0 0 hours temperature 4 0 0 hours history of 120c 120c 107℃ 1070 Squib 100g room 40 Ŋ 윤 တ ĸ භ Comparative Bxamples Bxamples [TABLE 15] 45

50

5	ory (3)	Appearance of gas generator after firing	No-trouble	No-trouble	No-trouble	filter breakage	filter breakage	filter breakage
16	erature hist	heating time	2min, 13sec.	2min, 15sec,	Zmin. Ogsec.	2 ain. 3 3 sec.	2 min. 4 9 sec,	2min. 44sec.
20	sins on Squib temp -Bonfire test-	presence or absence of synthetic resins	presence	presence	presence	absence	absence	absence
25	Effect of synthetic resins on Squib temperature history (3) -Bonfire test-	temperature history of Squib	room temperature	120t 100 hours	107°C 400 hours	room temperature	120t 100 hours	107°C 400 hours
30	Eff	No	7	80	Ĉ	2	8	6
35	[TABLE 16]			Examples			Comparative Examples	

Next, described are examples where a four-component spontaneous firing explosive composition according to the present invention (carbohydrates/oxyhalogenates/metal oxides /a synthetic resins) is contained in gas generant.

### Examples 10 through 18, 19 through 21

A spontaneous firing explosive composition was prepared as follows. 1.2 parts of said super fine powder of light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 74.8 parts of potassium chlorate (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.2 mm. After mixing, it was found that the surfaces of the potassium chlorate was coated with the magnesium oxide when observed through an optical microscope. Next, 1.0 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 23.0 parts of sucrose (Taito Corporation) having an average particle diameter of 0.05 mm. After mixing, it was found that the surface of the sucrose was coated with the magnesium oxide when observed through an optical microscope. The above mentioned total amount of potassium chlorate/magnesium oxide and sucrose/magnesium oxide were mixed with each other, to which 5.0 parts of silicon resin (Shin-etsu Silicon KE 441T; Shin-etsu Chemical Co., Ltd.) was added. The mixture was kneaded over 30 minutes. Thereafter, the mixture was stood at a room temperature over 48 hours to cure the silicon resin, thereby to obtain the spontaneous firing explosive composition.

This spontaneous firing explosive composition was placed in a mill of which diameter is 10 mm and press-molded under a load of 500 kilo-gram to obtain pellets of the gas generant, Weight of one pellet is approximately 0.6 gram. As shown in Fig. 7, the above mentioned pellets 35 gram were placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are: room temperature, 120°C x 100 hours and 107 °C x 400 hours, We used four containers to each types. Thereafter, as shown in Fig, 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the igniting agent container 40 having the igniting agent (boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 17 and Table 19. Differences in temperature histories during the 60-liter tank pressure-time test were slight. During the bonfire test, there were no differences in temperature histories found. An igniting time t (msec.) means a time up to start raising the pressure after an electrical current has finished flowing through the squib. Maximum pressure time means a time for pressure to become maximum. A heating time t in Table 12 means a time for the gas generator 60 to fire.

### Comparative Examples 10 through 18, 19 through 21

For comparison with the above mentioned examples, a gas generant was prepared without granulating with a silicon resin. As in the above, this was placed in a mill of which diameter is 10 mm and press-molded under a load of 500 kilo-gram to obtain pellets of the gas generant. Weight of one pellet is approximately 0.6 gram. As shown in Fig. 7, the above mentioned pellets 35 gram were placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are: room temperature, 120 °C × 100 hours and 107 °C × 400 hours. We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the igniting agents container 40 having the igniting agents(boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 18 and Table 19. During the 60-liter tank pressure-time test, there were a significant struggling in results. During the bonfire test, filter breakage was caused.

55

20

35

40

45

55

EP 0 665 138 A2

	1										- 7
		abnormal appeara- nce	none	none	none	none	none	попе	none	попе	поле
5		,ec.)	4	0	1	6	3	<u>r</u>	0		3
	_	maximum pressure time(msec)	49.	5.	e, .	47.	4.	5 2.	5 1.	46.	
	Bffect of synthetic resins on temperature history of gas generant pellet(1) 60-liter tank test	ma pr ti	4	4	5	4	4	2	5	4	5
10	pel	iii ire	က	6	5	6	₩.	3	9	8	3
	erant	maximum pressure KPa	206.	3 2.	175.	199.	2 2.	178.	202.	229.	180.
	gene	ii d	2	~3	1		2	1	2	2	
15	gas	ing ec)				-		2.	∞	io.	6
	ry of	igniting time t (msec)	6.2	5.8	6.4	6. 2	5.9	6. 2	5.8	5. 5	5. 9
	isto —	į									
20	sins on temperature hi 60-liter tank test	tor re	e i			a e			Ire		
	erat ank	genera test iperatu	room temperature	850	-40¢	room temperature	850	-40£	room temperature	855	-40¢
	tem ter t	gas generator test temperature	rc tempé	~	4-	r( temp(	. ~	7	temp	~	
25	ns on 30–1i			<u> </u>	<u> </u>		L			<u>                                     </u>	
	res i	presence or absence of synthetic resins		93			8			9	
	tic	presence or absence of nthetic res		presence			presence			presence	
30	ynthe	pres abse ynthe		H			Id.			甚	Ì
	of s	6		<del></del>							
	fect	ure of rant		ture			C OUTS		;	1075 400 hours	1
35	#	temperature history of gas generant		room temperature			120° 00 hours			D Loak	
		temp hist gas		ted		•	10		'	4 0	
		e £	97	=	12	13	14	12	16	17	82
40	-	-		<u> </u>	<u> </u>	1	J		L	<u> </u>	
	B 17.						Examples				
	[TABLE 17]	/					Exan				
45		<u> </u>	<u> </u>								

55

EP 0 665 138 A2

5		abnormal appearance	попе	none	none	none	попе	none	none	none	none
		m ire sec)	63	23	က	7	2	ιc	က	0	9
	(S)	maximum pressure time(msec)	5 7.	53.	7 1.	60.	5 1.	7 1.	56.	5 0.	7 0.
10	illet	tin B								6	
	nt pe	maximum pressure KPa	3.6	7.6	6.6		9.8	3. 3	2. 1	0. 6	2. 8
	nera	maximum pressur KPa	216.	277	16	201.	249	1.7	2 3	9 2	1.7
15	as ge								<u> </u>		
	of 8	igniting time t (msec)	<u>.</u>	6	1	က	4	8	6	က	
	Bffect of synthetic resins on temperature history of gas generant pellet(2)	igniti time t (mse	6.	5.	∞.	7.	မ်	∞.	7.	တ်	9.
50	his st—										
	ature k tes	gas generator test temperature	ture	2 ೭	ູນ	room temperature	ಬ್	ρ	room temperature	2 2	μ Q
	mper tan	as generator test temperature	room temperature	& 53	-40c	room	8	-40c	room nperat	8 5	-40c
25	on te liter	gas tem	te		<u>'</u>	‡ te		<b>'</b>	te		
	sins on temperature hi 60-liter tank test	surs									
	ည်း ' ပ	presence or absence of synthetic resins		ince			absence			absence	
30	cheti	presence or absence of		absence		į	abse			abse	
	synt	pr at syn									
	t t	, t		ę			2			ſS	
35	Effe	temperature history of gas generant		room temperature			1205 00 bours		i	1075 00 hours	
		aper istor		ro		,	0.0		,	1 0 4 0 0	
		b) te					<del>-</del>	·		٠,	
40		8	유	□	12	13	7	53	16	17	18
	181	/					ive	S			
	rable 18]						Comparative	Examples			!
45	E						Comi	<u></u>			

s (Table 19)	30	25	20	15	5
盃	ffect	Effect of synthetic resins on temperature history of gas generant pellet(3) -Bonfire test-	s on temperature hi -Bonfire test-	istory of gas	generant pellet(3)
	No	temperature history of gas generant	presence or absence of synthetic resins	heating time	Appearance of gas generator after firing
	19	room temperature	presence	lmin. 57 sec.	No-trouble
· · · · · · · · · · · · · · · · · ·	20	120¢ 100 hours	presence	2 min. 1 0 sec.	No-trouble
	21	107°C 400 hours	presence	2min. 12sec.	.No-trouble
	19	room temperature	авсепсе	2 min. 4 4 sec.	No-trouble
Comparative Examples	20	120¢ 100 hours	absence	2 min. 5 9 sec.	filter breakage
	12	107°C 400 hours	арѕепсе	2 min. 5 3 sec.	filter breakage

### Examples 22 through 30, 31 through 33

A spontaneous firing explosive composition was prepared as follows. 23.0 parts of wood powder having an average particle diameter of 0.05 mm was added to and mixed with 1.0 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.), to which 76.6 parts of potassium chlorate/magnesium oxide mixture prepared in said examples was added and mixed with each other, to which 5.0 parts of silicon resin was added. The mixture was kneaded over 30 minutes. Thereafter, the mixture was stood at a room temperature over 48 hours to cure the silicon resin, 24.0 parts of the above mentioned wood powder/potassium chlorate/magnesium oxide/silicon resin composition was mixed with 76.0 parts of spontaneous firing explosive composition based on sucrose/potassium chlorate/magnesium oxide/silicon resin prepared in said examples to obtain gas generant powder. As shown in Fig. 8, the above mentioned gas generant 35 gram was placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are: room temperature, 120 °C x 100 hours and 107 °C x 400 hours, We used four containers to each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the igniting agents container 40 having the igniting agents (boron/potassium nitrate) 1.0 gram and the above mentioned gas generant container 50. This gas generator 60 was used for test of a pressuretime with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 20 and

#### EP 0 665 138 A2

Table 22. Differences in temperature histories during the 60-liter tank pressure-time test were slight. During the bonfire test, there were no differences in temperature histories found.

## Comparative Examples 22 through 30, 31 through 33

A wood powder/sucrose/potassium chlorate/magnesium oxide mixture was prepared as a gas generant in the same manner and same ratio of the above mentioned examples 22 to 30 without silicon resin. As shown in Fig. 8, the above mentioned gas generant 35 gram was placed in the gas generant container 50 and sealed as shown in Fig. 6. Twelve containers such as the above mentioned generant containers 50 were ready. We applied three types of temperature histories. Here are: room temperature,  $120 \,^{\circ}\text{C} \times 100 \,^{\circ}\text{C} \times 100 \,^{\circ}\text{C} \times 400 \,^{\circ}\text{C} \times 100 \,^{\circ}\text{C} \times 100$ 

EP 0 665 138 A2

		abnormal appearance	попе	попе	попе	none	none	none	none	попе	none		
5		abnormal appearanc	<u>e</u>	잍	<u>e</u>	OH .	압	OU .	ou l	<u> </u>	<u></u>		
	a	maximum pressure time (msec)		. 2	4.6	7. 5	m 	6.0	6.4	7			
10	owder (1	max) pres	5 5.	50.	6.4	5.1	50.	9	ည	52.	9		
	erant j	maximum pressure KPa	211. 3	3. 7	დ	9.8	1, 6	7.3	2.2	9.9	6.5		
15	as gen	max pre	2 1	2.4	17	2 0	2 5	17	2 1	2 3	1 7		
	y of g	igniting time t (msec)	5. 4	5. 1	6.0	5. 2	4.9	6. 2	5. 5	5. 2	6. 6		
20	histor	ign t t (f	LIS.	ED.	9		7						
	rature nk test	erator t ture	m ature	5 5	<b>a</b> (	a ature	5 C	သူ(	m ature	855	) £		
25	Bffect of synthetic resins on temperature history of gas generant powder(1) 60-liter tank test	gas generator test temperature	room temperature	80	-40£	room temperature	80	-40£	room temperature	∞	-40£		
	esins c	or of es ins		ų			9			1ce			
30	etic r	presence or absence of synthetic resins		presence			presence		presence				
	f syntl	pro al syntj											
35	fect 0	ure of erant		n iture			hours		iours				
00	표	temperature history of gas generant		room temperature			1205 100 hours		107t				
			6)	- m	T			T	82	£3	e e		
40		<u> </u>	23	83	24	25	x	27	8	67	_ <u></u>		
	CTABLE 20)						Examples			٠			
45	[TA			· · · · · · · · · · · · · · · · · · ·			<b>E</b>						

55

EP 0 665 138 A2

5		abnormal appearance	none	попе	поле	none	none	попе	none	none	none	
10	vder (2)	maximum pressure time(msec)	63.2	55.4	74.6	65.7	55.6	89.2	64.9	6 0. 9	82.7	
15	s generant po	maximum pressure KPa	202.1	241.5	158.2	190, 2	227. 4	154.6	188.1	200.3	160.1	
20	istory of ga -	igniting time t (msec)	6.6	4.9	8.8	7.9	4.8	10.3	7.8	6.5	11.3	
25	sins on temperature hi -60-liter tank test-	gas generator test temperature	room temperature	855	-40£	room temperature	358	-40£	room temperature	855	-40c	
30	Bffect of synthetic resins on temperature history of gas generant powder(2) 60-liter tank test	presence or absence of synthetic resins		absence		-	absence		absence			
35	Bifect of	temperature history of gas generant		temperature		\$ 0 7	100 hours		107°C 400 hours			
40		No	83	23	24	22	92	27	78	53	R	
45	KTABLE 21)						Comparative	Examples		•		

#### EP 0 665 138 A2

	ල	<b>1 1</b> .				9	5	9
5	ромдег	Appearance of gas generator after firing	No-trouble	No-trouble	No-trouble	filter breakage	filter breakage	filter breakage
	gas generant powder(3)	Appear gas ge after	%o-tı	¥o−t;	No-ti	filter	filter	filter
10	gas g			· ·				
15	synthetic resins on temperature history of -Bonfire test-	heating time	1min, 59sec,	2 min. O 7 sec.	. 2 min. O 6 sec.	2min, 4 1 sec.	2 min. 3 3 sec.	2min, 50sec,
15	re hi	SII						
	eratu	e or of resi	ince	nce	nce	92	ıce	ace.
20	on temp est-	presence or absence of synthetic resins	presence	presence	presence	absence	авѕепсе	absence
	ins (	sy.						
	ic resins on t -Bonfire test-	it it	<del>စ</del>	တ္သ	rs	re	ខន	rs
25	theti	temperature history of gas generant	room temperature	120 to 0 to	107°C 400 hours	room temperature	120°C 00 hours	1075 400 hours
		tempe histo gas (	ro	1 2	1 0 4 0 0	r	100	1 (4 0 (
30	Bffect of							
	Bffe	2	31	32	33	19	20	21
	ZZ.			les			ative ples	
35	KTABLB 221			Examples			Comparative Examples	

Next, described are examples where a spontaneous firing explosive composition according to the present invention (carbohydrates/oxyhalogenates/metal oxides/synthetic resins) was contained in the igniting

#### Examples 34 through 42, 43 through 45

A spontaneous firing explosive composition was prepared as follows. 1.2 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) was added to and mixed with 74.8 parts of potassium chlorate (reagent; Wako Pure Chemical Industries Co., Ltd.) having an average particle diameter of 0.2 mm. After mixing, it was found that the surfaces of the potassium chlorate were coated with the magnesium oxide when observed through an optical microscope, Next, 1.0 parts of said light magnesium oxide (reagent; Wako Pure Chemical Industries Co., Ltd.) were added to and mixed with 23.0 parts of sucrose (Taito Corporation) having an average particle diameter of 0.05 mm. After mixing, it was found that the surfaces of the sucrose were coated with the magnesium oxide when observed through an optical microscope. The above mentioned total amount of potassium chlorate/magnesium oxide and sucrose/magnesium oxide were mixed with each other, to which 5.0 parts of silicon resin (Shin-etsu Silicon KE 441T; Shin-etsu Chemical Co., Ltd.) were added. The mixture was kneaded over 30 minutes, Thereafter, the mixture was stood at a room temperature over 48 hours to cure the silicon resin, thereby to obtain the spontaneous firing explosive composition.

30

35

40

45

50

55

#### EP 0 665 138 A2

As shown in Fig. 9, the above mentioned spontaneous firing explosive composition 2.0 gram was placed in the igniting agents container 40 and sealed. Twelve containers such as the above mentioned igniting agents containers 40 were ready. We applied three types of temperature histories. Here are: room temperature, 120 °C × 100 hours and 107 °C × 400 hours. We used four containers to said each types. Thereafter, as shown in Fig. 1, the gas generator 60 made of the aluminum casing was assembled. The gas generator 60 contains the squib 10 having zirconium/potassium perchlorate 120 milli-gram, the gas generant container 50 having the gas generant based on sodium azide 55 gram, and the igniting agents container 40 having the above mentioned spontaneous firing explosive composition. This gas generator 60 was used for test of a pressure-time with a 60-liter tank and a heating test with firewood (bonfire test). The results are given in Table 23 and Table 25. Differences in temperature histories during the 60-liter tank pressure-time test were slight. During the bonfire test, there were no differences in temperature histories found. An igniting time t (msec.) means a time up to start raising the pressure after an electrical current has finished flowing through the squib. Maximum pressure time means a time for pressure to become maximum. A heating time t means a time for the gas generator 60 to fire.

### Comparative Examples 34 through 42, 43 through 45

For comparison with said examples, a sucrose /potassium chlorate/magnesium oxide was prepared as igniting agents without synthetic resins. This igniting agents were placed in the igniting agents container in the same manner of said examples, Twelve containers such as the above mentioned igniting agents containers 40 were ready. We applied three types of temperature histories, Here are: room temperature, 120 °C × 100 hours and 107 °C × 400 hours. We used four containers to said each types. Thereafter, as shown in Fig. 1, the gas generator was assembled with the same specifications of said examples except for the igniting agents. This gas generator is used to conduct the same assessment tests as in said examples. The results are given in Table 24 and Table 25. During the 60-liter tank pressure-time test, there was a significant struggling in results. During the bonfire test, filter breakage was caused.

55

EP 0 665 138 A2

No history of igniting age igniting age room 34 room 35 temperature 36	at ts	presence or absence of synthetic resins presence	gas generator test temperature room temperature 855	igniting time t (msec) 5. 1 5. 9	maximum pressure KPa 143.4 176.2	maximum pressure time(msec) 5 3. 3 4 5. 6	abnormal appearance none none
		presence	room temperature 855	1 1		1 1	none none
		presence	8 5 c		76.	l 1	none
38	room temperature		∴ 4 0 ℃		27.		none
		-	-				
37			room temperature	5.3	147.8	54. 1	попе
Examples 38 100	120c 00 hours	presence	855	4. 5	170.9	46.6	none
33			-40£	6.3	120.5	65.2	попе
07			room temperature	5. 1	141.7	56. 5	попе
107°C 41 400 hours	hours	presence	855	4. 3	177.2	46.1	попе
42		1	-40£	6. 1	125.5	66.3	попе

55

EP 0 665 138 A2

		1 130e									
5		abnormal appearance	none	попе	попе	попе	попе	none	попе	กดขอ	none
10	istory (2)	maximum pressure time(msec)	55. 5	41, 4	73.6	59.8	42.3	83. 1	57.3	43.9	82.4
15	emperature hi	maximum pressure KPa	146.1	177.3	109.3	140.1	168.3	105.2	140.8	165.5	9 9.8
10	ing agents t -	igniting time t (msec)	4.9	4. 1	7.5	6.0	4.8	8.8	6. 2	5.0	9. 2
20 25	hetic resins on igniti 60-liter tank test-	gas generator test temperature	room temperature	852	-40c	room temperature	850	-40£	room temperature	852	-40c
30	Effect of synthetic resins on igniting agents temperature history (2) 60-liter tank test	presence or absence of synthetic resins		absence			absence			absence	
35	m	temperature history of igniting agents		temperature		*** O 0 *	120C		\$ 20 -	101C 400 hours	
40		% %	34	35	88	37	38	ç	49	41	42
45	[TABLE 24]						Comparative	kxamp les		>	

	ļ				I			
5	nistory (3)	Appearance of gas generator after firing	No-trouble	No-trouble	No-trouble	filter breakage	filter breakage	filter breakage
10	temperature h	heating time	2 min. O 1 sec.	2 min. 0 6 sec.	1 min. 5.9 sec.	2 min. 2 4 sec.	2min, 32sec.	2 min, 4 O sec.
20	on igniting agents -Bonfire test-	presence or absence of synthetic resins	presence	presence	presence	авзепсе	авѕепсе	авзепсе
25	Bffect of synthetic resins on igniting agents temperature history (3) Bonfire test	temperature history of igniting agents	room temperature	120°C 100 hours	107°C 400 hours	room temperature	120°C 100 hours	1070 400 hours
30	fect	No	43	44	45	43	44	45
35	TABLE 251 Bf			Examples			Comparative Examples	

Next, described in conjunction with Table 26 are various exemplified combinations of carbohydrates, metal oxides and synthetic resins in a spontaneous firing explosive composition of carbohydrates/oxyhalogenates/metal oxides/synthetic resins,

### Examples 46 through 51, Comparative Example 46 through 51

- The combination given in Table 26 was mixed at the following ratio to prepare an explosive composition.
  - Sucrose (Taito Corporation) 23.0% by weight (Example 46 and 47, Comparative Examples 46 and 49)
  - Dextrin (reagent; Kishida Chemical Industries Co., Ltd.) 23.0% by weight (Examples 48 and 49, Comparative Examples 47 and 50)
- Cellulose (reagent; Wako Pure Chemical Industries Co., Ltd.) 23.0% by weight (Examples 50 and 51, Comparative Examples 48 and 51)
  - Potassium Chlorate (reagent; Kanto Chemical Co., Ltd.) 74.0% by weight (Examples 46 through 51) and 77.0% by weight (Comparative Examples 46 through 51)
  - MgO (reagent; Wako Pure Chemical Industries Co., Ltd.) 2.0% by weight (Examples 46 through 48 and 50, Comparative Example 46)
    - ZnO (reagent; Wako Pure Chemical Industries Co., Ltd.) 2.0% by weight (Example 49, Comparative Example 47)
      - CaO (reagent; Wako Pure Chemical Industries Co., Ltd.) 2.0% by weight (Example 51, Comparative

Example 48)

10

15

30

35

40

45

50

55

Silicon Resin (One-component room-temperature curable type) (Trade Name "Shin-etsu Silicon KE 441T" available from Shin-etsu Chemical Co., Ltd.) (Examples 46, 48 and 50, Comparative Examples 49 through 51)

Urethane Resin (Trade Name "Hi-Bon 4601" available from Hitachi Kasei Polymer Co., Ltd.) (Example 47)

Butyl Rubber (Trade Name "Hi-Bon 1010A" available from Hitach Kasei Polymer Co., Ltd.) (Example 49)

Polyester Resin (Trade Name "Hi-Bon 7031L" available from Hitachi Kasei Polymer Co., Ltd.) (Example 51).

The mixture was made by means of two steps mixing. At first, carbohydrates and potasslum chlorate are respectively mixed up with metal oxides and then these mixtures are mixed together. Thereafter, the synthetic resins were added thereto, which was kneaded and granulated over 30 minutes and was stood at a room temperature over 48 hours for curing the resins.

The resultant spontaneous firing explosive compositions were subjected to measurements on the generated pressure and the time when said generated pressure rises up till maximum by using a test vessel obtained by attaching a pressure sensor to a stainless vessel having an inner volume of 1 liter, in which the spontaneous firing explosive composition 8 gram was burned in the form of granule (1-liter tank test).

To ignite the spontaneous firing explosive composition, a squib having firing agent 0.6 gram contained of a boron/potassium nitrate and lead styphnate fuse heads were used. The igniting time means a time interval from time when electrical current has finished flowing through the squib to time of starting raising the pressure.

The spontaneous firing explosive compositions were applied with temperature history of 120 °C × 100 hours to determine the heat aging properties. A spontaneous firing temperature of the spontaneous firing explosive compositions was measured by using a differential thermal analyzer (Type DSC 220: Seiko Instruments Inc.). The results of the above tests are summarized in Table 26.

## EP 0 665 138 A2

	ı							·	<del></del> 1			т		-							
5		100 hours 120 C	01040440000	firing	temperature	(2)	175	174	205	200	224	226	193	231	2 5.5 5.5						
		properties after 100 hours 120°C	and in	pressure		(atm)	43,0	39. 7	37.0	36.4	26, 2	27.0	39.0	30.1	27.3						
70		propert		propert	propert		pressure	tine	(msec)	3.7	4.1	44	42	48	47	44	53	6.2	no-ignite	no-ignite	na-ignite
16		rties		spontaneous firing	temperature	(£)	173	174	203	199	222	2 2 5	188	220	248	169	195	2.19			
		initial properties	,	pressure		(atm)	42.6	39.5	36.0	35.3	27.3	31.1	40.5	34.2	29.9	43.7	34.6	28.0			
20		iui		pressure	tine	(asec)	38	4.0	4.5	43	4.9	5.1	43	5.1	5.7	2.5	33	4.8			
25			synthetic	resin	type		Silicon	Urethane	Silicon	Butyl Rubber	Silicon	Polyester	absence	absence	absence	Silicon	Silicon	Silicon			
30			xides	average	particle diameter	(mm)	≤0.001	≤0.001	≤0, 001	0.03	≤0.001	0.01	≤0.001	0.03	0.01						
			metal oxides		type		Mgo	MgO	MgO	2 n.o	MgO	CaO	Mgo	2 n O	CaO	арзепсе	absence	absence			
35		components	potassium	chlotate average	particle	(ma)	0. 2	0. 2	0. 1	0. 1	0.1	0.1	0, 2	0. 1	0. 1	0. 2	0. 1	0.1			
40		совр	drates	average	particle	(E)	0.02	0.02	0.01	0.01	0.03	0.03	0,02	0.01	0.03	0.02	0.01	0.03			
			carbohydrates		+406	2	sucrose	sucrose	dextrin	dextrin	powder cellulose	powder cellulose	sucrose	dextrin	powder cellulose	sucrose	dextrin	powder cellulose			
45		<b></b>	L	1			\$3	127	\$	5	居	51	97	47	83	<b>9</b>	B	Ę			
50	[TABLE 26]			_						Examples					Comparative	Examples		,			

In Examples 46 through 51, there were no significant differences in properties between the initial properties and those after heat aging at 120 °C for 100 hours because the conditions met the specifications according to the present invention. In particular, reproducibility of the spontaneous firing temperature was excellent.

In Comparative Examples 46 through 48, the spontaneous firing temperatures were increased because there were no synthetic resins contained. The spontaneous firing temperatures were further increased after

the heat aging at 120 °C for 100 hours. In Comparative Examples 49 through 51, non-igniting were found after the heat aging at 120 °C for 100 hours because there were no metal oxides contained. In addition, the spontaneous firing temperature couldn't be measured. For the state after heat aging, no changes were found in Examples and Comparative Examples 46 through 48 while Comparative Examples 49 through 51 resulted in color change into black-brown due to effect of heat.

As apparent from the above, the spontaneous firing explosive composition according to the present invention has a spontaneous firing function in a specific high-temperature range and kept a stable burning capability after the heat aging at 120 °C for 100 hours.

As described in detail above, the gas generator for air bag according to the present invention requires no preparation of a specific container space in a casing by means of containing a spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates and metal oxides in at least one of the squib, the igniting agents and the gas generant, and it is thus possible to maintain stable properties for a long time with safety and a spontaneous firing function at a low temperature up to 220 °C without particular considerations on the heat conductivity between the casing, so that it is optimum as the gas generator with the casing of a light alloy material or the like of which mechanical strength will be deteriorated when being subjected to high temperature environments. When the heat conductivity from outside is not so good, it is possible to further ensure the spontaneous firing function at a low temperature up to 200 °C by means of containing a spontaneous firing explosive composition consisting of carbohydrates, oxyhalogenates, metal oxides and synthetic resins.

In particular, when the squib contains the spontaneous firing explosive composition according to the present invention as compared with a case where it is contained in the gas generant or the firing agents, this eliminates a fear of the explosive left in the casing without igniting of the squib after the spontaneous firing of said explosive composition. In addition, in case of prior art such as a spontaneous firing explosive composition also serving as initiating agents, the bridge wire contacting therewith is corroded due to acidic substances generated as a result of deterioration with time. So, there's a fear for an incorrect operation because of the squib not initiated upon a normal operation. While in case of the present invention, there's no fear such as said trouble. Further, the present invention can find various applications as the squib having the spontaneous firing function.

In particular, when the gas generant contains the spontaneous firing explosive composition according to the present invention, no toxic gas is generated after it absorbs water as compared with conventional ones based on sodium azide. It can be a gas generator containing a novel gas generant which is capable of maintaining stable properties during exposure to high temperature environments for a long time and which has an adequate burning rate in a normal operation.

Further, when the igniting agents contains the spontaneous firing explosive composition according to the present invention, this is possible to obtain a more excellent high-temperature stability and a more sufficient burning rate than ones of the prior art such as a spontaneous firing explosive composition also serving as igniting agents.

The present invention is a gas generator for air bag comprises a spontaneous firing explosive composition in which at least one of a squib 10, igniting agents 41 and a gas generant 51 contained in a casing 27 or 28 formed of a light alloy material or the like, a spontaneous firing explosive composition consists of carbohydrates, oxyhalogenates and metal oxides and alternatively of carbohydrates, oxyhalogenates, metal oxides and a synthetic resin. The spontaneous firing explosive composition has a spontaneous firing property in temperatures range of 165-220 °C or of 165-200 °C. The carbohydrates is a gaseous component and the oxyhalogenates is an oxygen supplying component. Accordingly, a firing temperature in a relatively low temperatures range of 165-220 °C or of 165-200 °C may be selected depending on combinations of the two. The metal oxides is a heat stabilizer and the synthetic resin is a binder for use in granulating the spontaneous firing explosive composition.

#### Claims

50

20

 A gas generator for air bag comprising a squib or one or more igniting agents and a gas generant contained therein, wherein at least one of said squib, said igniting agents and said gas generant contains a spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates and metal oxides.

55

2. A gas generator for air bag as claimed in Claim 1, wherein said squib, said igniting agents, or said gas generator is contained in a casing made of a light alloy material such as an aluminum alloy, wherein said spontaneous firing explosive composition being spontaneously fired at temperatures from 165 °C

to 220 °C.

5

20

25

30

35

40

45

- 3. A gas generator for air bag as claimed in Claim 1 containing said spontaneous firing explosive composition wherein said carbohydrates of which an average particle diameter from 0.5 mm to 0.0001 mm, said oxyhalogenates of which an average particle diameter from 1.0 mm to 0.0001 mm, said metal oxides of which an average particle diameter from 0.5 mm or smaller.
- 4. A gas generator for air bag as claimed in Claim 1, wherein said carbohydrates, said oxyhalogenates and said metal oxides in said spontaneous firing explosive composition are respectively from 95.0% to 1.0% by weight, from 95.0% to 1.0% by weight and from 30.0% to 0.01% by weight.
  - 5. A gas generator for air bag as claimed in Claim 1, wherein at least one of said carbohydrates and said oxyhalogenates in said spontaneous firing explosive composition is coated with said metal oxides.
- 15 6. A gas generator for air bag as claimed in Claim 1, wherein said carbohydrates, said oxyhalogenates and said metal oxides in said spontaneous firing explosive composition were mixed uniformly.
  - 7. A gas generator for air bag as claimed in Claim 1 containing said spontaneous firing explosive composition, wherein said carbohydrates is sucrose, wherein said oxyhalogenates is a single or a mixture of chlorate, perchlorate, bromate, perbromate, iodate and periodate and where in said metal oxides is a single or a mixture of calcium oxide, magnesium oxide and zinc oxide.
  - 8. A gas generator for air bag comprising a squib or one or more igniting agents and a gas generant contained therein, wherein at least one of said squib, said igniting agents and said gas generant contains a spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates, metal oxides and a synthetic resins.
  - 9. A gas generator for air bag as claimed in Claim 8, wherein said squib, said igniting agents, or said gas generator is contained in a casing made of a light alloy material such as an aluminum alloy, wherein said spontaneous firing explosive composition being spontaneously fired at a temperatures from 165 °C to 200 °C.
  - 10. A gas generator for air bag as claimed in Claim 8 containing said spontaneous firing explosive composition wherein the carbohydrates of which an average particle diameter of from 0.5 mm to 0.0001 mm, said oxyhalogenates of which an average particle diameter of from 1.0 mm to 0.0001 mm, said metal oxides of which an average particle diameter of from 0.5 mm or smaller.
  - 11. A gas generator for air bag as claimed in Claim 8, wherein said carbohydrates, said oxyhalogenates, said metal oxides and said synthetic resins in said spontaneous firing explosive composition are respectively from 95.0% to 1.0% by weight, from 95.0% to 1.0% by weight, from 30.0% to 0.01% by weight and from 0.5% to 20.0% by weight.
  - 12. A gas generator for air bag as claimed in Claim 8, wherein at least one of said carbohydrates and said oxyhalogenates in said spontaneous firing explosive composition are coated with said metal oxides.
  - 13. A gas generator for air bag as claimed in Claim 8, wherein said carbohydrates, the said oxyhalogenates and said metal oxides in said spontaneous firing explosive composition were mixed uniformly.
- 14. A gas generator for air bag as claimed in Claim 8, wherein a mixture of said carbohydrates, said oxyhalogenates and said metal oxides is granulated by said synthetic resins.
  - 15. A gas generator for air bag as claimed in Claim 8 containing said spontaneous firing explosive composition, wherein said carbohydrates is sucrose, where in said oxyhalogenates is a single or a mixture of chlorate, perchlorate, promate, perbromate, iodate and periodate, wherein said metal oxides is a single or a mixture of calcium oxide, magnesium oxide and zinc oxide and wherein said synthetic resins is any one of silicon resins, urethane resins, polyesters, acrylic resins and butyl rubbers.

15

20

25

30

35

40

45

55

#### EP 0 665 138 A2

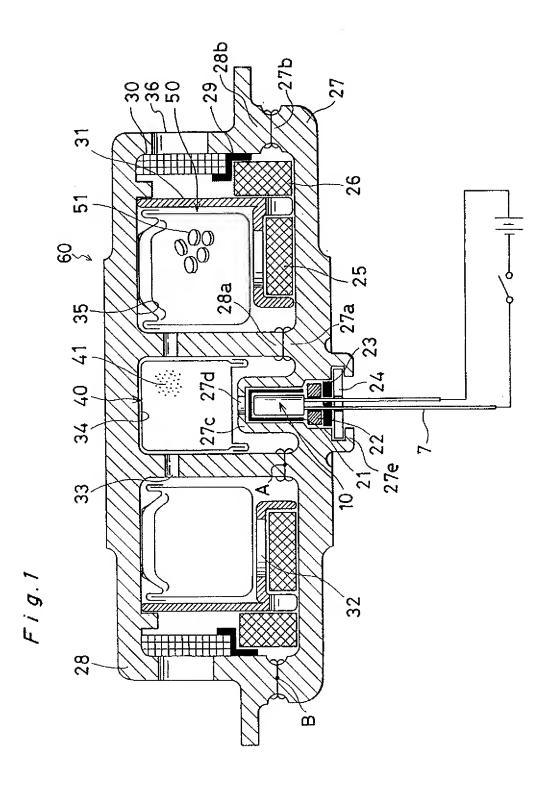
- 16. A squib comprising a magazine which is formed with a squib cup and a squib plug and is sealed; a pair of electrode lead pins penetrating through said squib plug to said magazine; a bridge wire connected to ends of said electrode lead pins; and a explosive contained in said magazine; said explosive containing a spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates and metal oxides.
- 17. A squib as claimed in Claim 16, wherein said explosive is in a layer structure consisting of initiating agents contacting with the bridge wire and the spontaneous firing explosive composition contacting with said initiating agents.
- 18. A squib comprising a magazine which is formed with a squib cup and a squib plug and is sealed; an electrode lead pins penetrating through said squib plug to said magazine; a bridge wire connected to ends of said electrode lead pins; and an explosive contained in said magazine; said explosive containing a spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates, metal oxides and a synthetic resin.
- 19. A squib as claimed in Claim 18, wherein said explosive is in a layer structure consisting of initiating agents contacting with the bridge wire and the spontaneous firing explosive composition contacting with said initiating agents.
- 20. A gas generator for air bag in which a squib is held by a casing made of a light metal material such as an aluminum alloy;

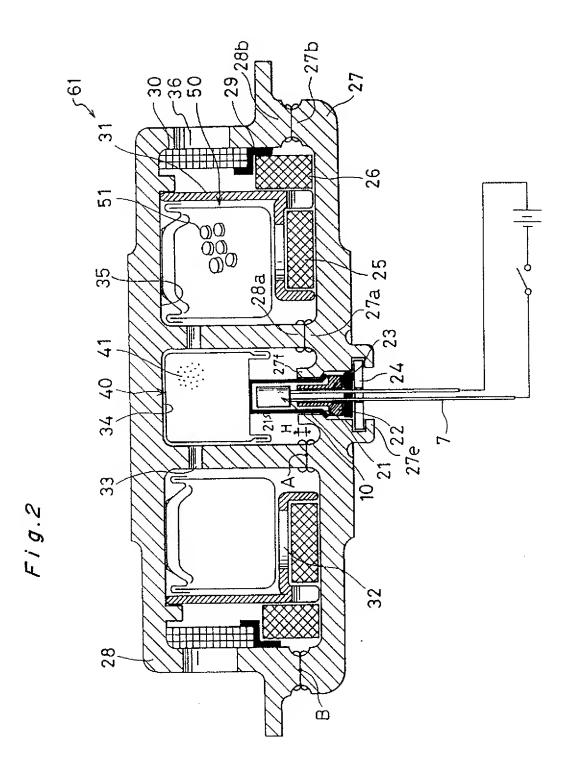
said squib comprising a magazine which is formed with a squib cup and a squib plug and is sealed, a pair of electrode pins penetrating through said squib plug to said magazine, a bridge wire connected to ends of said electrode lead pins and an explosive contained in said magazine,

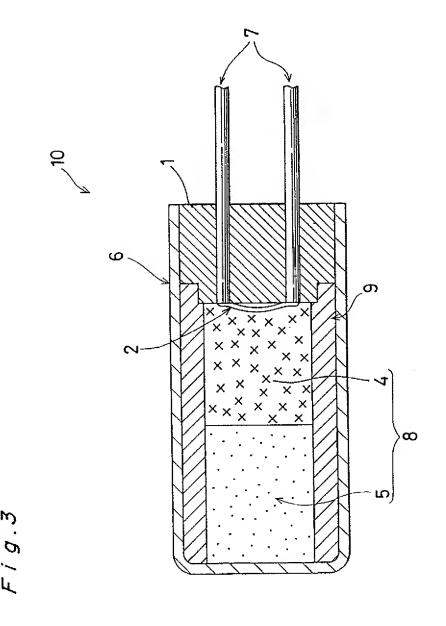
said explosive being in a layer structure consisting of initiating agents contacting with said bridge wire and said spontaneous firing explosive composition contacting with said initiating agents; said spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates, metal oxides and a synthetic resins, a portion of said squib corresponding to the spontaneous firing explosive composition being exposed within said casing without contact to said casing.

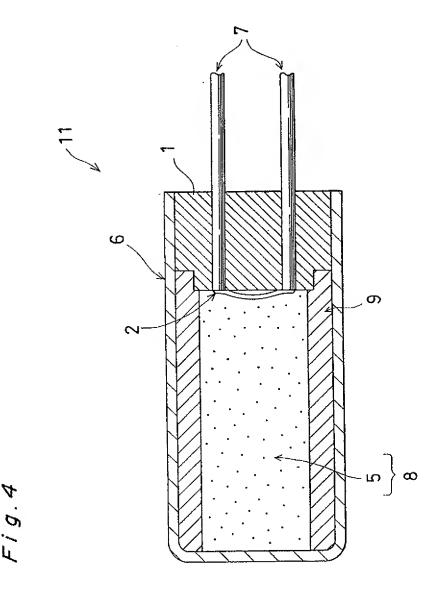
- 21. A gas generator for air bag comprising a casing formed of a light metal material such as aluminum alloy with an upper casing member and a lower casing member having an inner cylinder and an outer cylinder respectively, which are opposed to and frictional welded with each other corresponding to said inner cylinders and outer cylinders each other and having a center space within said inner cylinder and an outer space surrounded by said inner cylinder and said outer cylinder; igniting agents and a squib being arranged within said center space and a gas generant and a filter being arranged within said outer space.
- an outer surface of said squib being coated with an electrically insulating material, said coated squib being inserted into said casing and fixed thereto and containing the spontaneous firing explosive composition consisting of carbohydrates, oxyhalogenates, metal oxides and a synthetic resin.
- 22. A gas generator for air bag as claimed in Claim 21, wherein said squib is inserted into a cylinder-shaped boss projected from outside of said casing into said center space and fixed thereto, said cylinder-shaped boss being larger in height than the portion of said friction welding.
- 23. A spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates and metal oxides.
- 24. A spontaneous firing explosive composition as claimed in Claim 23, wherein said spontaneous firing explosive composition being spontaneously fired at temperatures from 165 °C to 220 °C.
  - 25. A spontaneous firing explosive composition as claimed in Claim 23, wherein said carbohydrates is sucrose, wherein said oxyhalogenates is a single or a mixture of chlorate, perchlorate, bromate, perbromate, iodate and periodate and wherein said metal oxides is a single or a mixture of calcium oxide, magnesium oxide and zinc oxide.

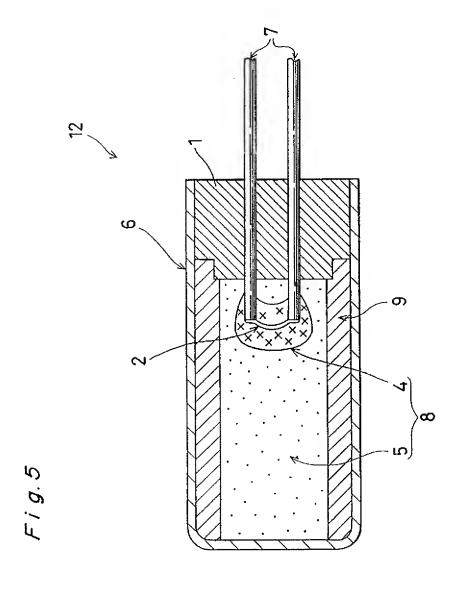
- 26. A spontaneous firing explosive composition comprising carbohydrates, oxyhalogenates, metal oxides and a synthetic resin.
- 27. A spontaneous firing explosive composition as claimed in Claim 26, wherein said carbohydrates is sucrose, wherein said oxyhalogenates is a single or a mixture of chlorate, perchlorate, bromate, perbromate, iodate and periodate, where in said metal oxides is a single or a mixture of calcium oxide, magnesium oxide and zinc oxide and wherein said synthetic resin is any one of silicon resins, urethane resins, polyesters, acrylic resins and butyl rubbers.



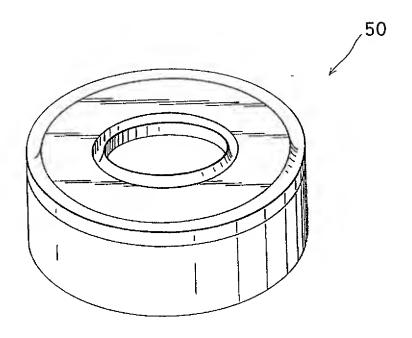








F i g. 6



F i g. 7

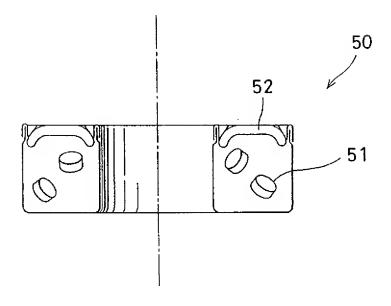
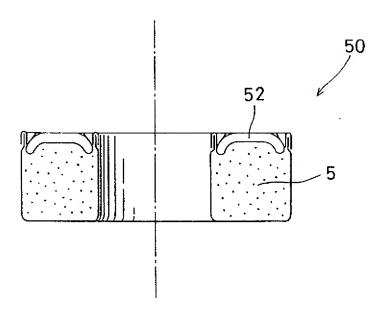


Fig.8



F i g. 9

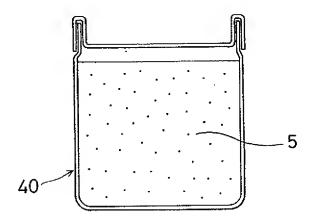


Fig. 10

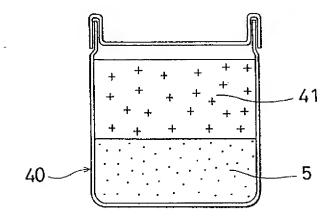


Fig.11

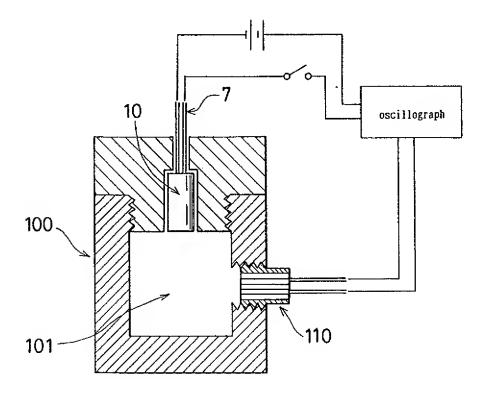


Fig.12

